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# Monohalogenobenzoylhydrazones
# III. Synthesis and Structural Studies of Pt(II), Pd(II) and Rh(III) Complexes of Di-(2-pyridyl)ketonechlorobenzoyl Hydrazones

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## Abstract

In a sequence to our earlier reports of transition metal complexes with benzoyl- and chlorobenzoyl-di-(2-pyridyl)ketohydrazone, we here report the isolation of palladium(II), platinum(II) and rhodium(III) complexes with the same ligands and their characterization by chemical analysis, as well as magnetic and spectral studies, in order to evaluate the stereochemistry of the ligand around the metal ions. In these complexes the ligands behaved as terdentate, coordination occurring through the carbonyl and azomethine groups, as well as the nitrogen atom of the pyridyl group. Consequently, the Pd(II) and Pt(II) complexes are formulated as square-pyramidal monomers, whereas in Rh(III) complexes an octahedral environment around the metal is proposed.

## Introduction

In recent years an increasing number of metal complexes of hydrazones has been studied due to the established biological activity of this class of compounds and novel structural features presented by the metal complexes of such ligands [1–5]. Moreover, the ligating properties of several heterocyclic nitrogen-containing hydrazones and their metal complexes have been extensively studied [6–9], as these ligands can act as bidentate and/or terdentate. In our laboratory, the coordination chemistry of several hydrazone derivatives of heterocyclic nitrogen containing ketones has been studied and reported [10–17]. This work has been extended to the hitherto uninvestigated benzoyl- and chlorobenzoyl-di-(2-pyridyl)ketohydrazonato complexes of platinum group metal ions because there are as many as five potential donor sites and a possibility of keto–enol tautomerism which may be expected to lead to varied bonding and stereochemical behaviour in the complexes. Aside from showing interesting physicochemical properties, complexes of these elements are of significant interest because of their potential antitumor activity. Consequently, the results of our investigations on the synthesis and structural studies of Pd(II), Pt(II) and Rh(III) complexes with the title ligands are reported in the present paper. The complexes have been isolated in the solid state and structures have been assigned tentatively on the basis of their elemental analyses, as well as their spectral and magnetic properties.

## Experimental

### *Physical Measurements*

IR spectra were recorded in the 4000–250 $cm^{-1}$ region on a Perkin-Elmer 467 spectrophotometer using KBr pellets or Nujol mulls. Electronic spectra in dimethylformamide (DMF) solutions were obtained on a Cary 17DX spectrophotometer. Mass spectra were measured on a RMU-6L Hitachi Perkin-Elmer mass spectrometer with ionization source of T-2p type operating at 70 eV. Conductivity measurements were done in a Wheatstone bridge Model RC $216B_2$ using $10^{-3}$ M solutions in DMF. Melting points were determined with a Büchi apparatus and are uncorrected. The elemental analysis of carbon, nitrogen and hydrogen was performed on a Perkin-Elmer 240B Elemental Analyzer. Chlorine was determined by combustion after Schöniger followed by titration with silver nitrate. Palladium, platinum and rhodium were determined according to published methods [18].

### *Starting Materials*

All solvents were of reagent grade and were used without further purification in synthetic work. The ligands benzoyl-, and *o*-, *m*- and *p*-chlorobenzoyl-di-(2-pyridyl)ketohydrazone (abbreviated as DBH, DoClBH, DmClBH and DpClBH, respectively) were prepared and recrystallized as previously reported [13]. All the other reagents were obtained commercially.

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TABLE I. Analytical Data for the new Pd(II), Pt(II) and Rh(III) Complexes[a]

| Compound | Yield (%) | Melting point[b] (°C) | Elemental analyses (%) | | | | |
|---|---|---|---|---|---|---|---|
| | | | C | N | H | Cl | M[c] |
| $PdCl_2$(DBH) | 58 | 278–280d | 45.10<br>(45.07) | 11.50<br>(11.68) | 2.89<br>(2.94) | 14.60<br>(14.78) | 22.00<br>(22.18) |
| $PdCl_2$(DoClBH) | 42 | 246–248d | 42.00<br>(42.05) | 10.80<br>(10.89) | 2.40<br>(2.55) | 20.60<br>(20.68) | 20.41<br>(20.69) |
| $PdCl_2$(DmClBH) | 65 | 286–288d | 41.90<br>(42.05) | 10.95<br>(10.89) | 2.50<br>(2.55) | 20.51<br>(20.68) | 20.50<br>(20.69) |
| $PdCl_2$(DpClBH) | 62 | 290–292d | 41.87<br>(42.05) | 10.70<br>(10.89) | 2.48<br>(2.55) | 20.30<br>(20.68) | 20.55<br>(20.69) |
| $PtCl_2$(DBH) | 49 | 258–260d | 37.81<br>(38.00) | 9.69<br>(9.85) | 2.41<br>(2.48) | 12.31<br>(12.47) | 34.27<br>(34.32) |
| $PtCl_2$(DoClBH) | 38 | 230–232d | 35.80<br>(35.86) | 9.10<br>(9.29) | 2.15<br>(2.17) | 17.55<br>(17.64) | 32.10<br>(32.36) |
| $PtCl_2$(DmClBH) | 51 | 262–264d | 35.71<br>(35.86) | 9.17<br>(9.29) | 2.26<br>(2.17) | 17.40<br>(17.64) | 32.20<br>(32.36) |
| $PtCl_2$(DpClBH) | 57 | 276–278d | 35.58<br>(35.86) | 9.31<br>(9.29) | 2.31<br>(2.17) | 17.50<br>(17.64) | 32.17<br>(32.36) |
| $RhCl_3$(DBH) | 65 | 254–256d | 42.14<br>(42.25) | 10.59<br>(10.95) | 2.85<br>(2.74) | 20.51<br>(20.80) | 19.95<br>(20.13) |
| $RhCl_3$(DoClBH) | 47 | 318–320d | 38.99<br>(39.58) | 10.47<br>(10.26) | 2.45<br>(2.38) | 25.78<br>(25.99) | 18.55<br>(18.86) |
| $RhCl_3$(DmClBH) | 53 | 261–263d | 39.54<br>(39.58) | 10.22<br>(10.26) | 2.65<br>(2.38) | 25.60<br>(25.99) | 18.68<br>(18.86) |
| $RhCl_3$(DpClBH) | 67 | 280–282d | 41.29<br>(39.58) | 10.57<br>(10.26) | 2.69<br>(2.38) | 25.75<br>(25.99) | 18.26<br>(18.86) |

[a] Calculated values in parentheses. [b] d = decomposition. [c] M = Pd, Pt or Rh.

## *Preparation of the Complexes*

### *Palladium(II) complexes*

$PdCl_2$ was suspended in ethanol and treated with a 1:1 mole ratio of the appropriate ligand dissolved in the same solvent. The reaction mixture was stirred for 3–6 h at room temperature. During this period an amorphous orange precipitate of the corresponding palladium(II) complex began to appear. On standing for several hours, a microcrystalline solid was formed which was filtered off, washed with ethanol and ether and dried in vacuum. Recrystallization was carried out from methanol. The yields in this procedure were about 60%.

### *Platinum(II) complexes*

An aqueous solution of $K_2PtCl_4$ was treated with the appropriate ligand (1:1 mole ratio) dissolved in ethanol. In the resulted clear solution a brownish precipitate was separated which was filtered off, washed with ethanol and ether and dried in vacuum over $P_2O_5$. Recrystallization was carried out by dissolving the solid in DMF and reprecipitating with ether. The yields in this procedure were about 50%.

### *Rhodium(III) complexes*

$RhCl_3 \cdot 3H_2O$ was dissolved in ethanol and treated with a 1:1 mole ratio of the appropriate ligand dissolved in chloroform. The solution was stirred for 2 h whereupon a yellow precipitate was formed which was filtered, washed with ether and dried in vacuum. Recrystallization was carried out from methanol. The yields in this procedure were about 60%.

## **Results and Discussion**

Reaction of palladium(II), platinum(II) and rhodium(III) salts with the ligands investigated, namely benzoyl- and chlorobenzoyl-di-(2-pyridyl)-ketohydrazone, afforded microcrystalline complexes of 1:1 metal:ligand stoichiometry which were found to be quite stable in the atmosphere. The results of the elemental analyses for the complexes are given in Table I. The complexes are insoluble in water and common organic solvents such as chloroform, acetone, benzene and nitrobenzene, but are slightly soluble in ethanol and soluble in coordinating solvents such as DMF and DMSO. The insufficient solubility of the complexes in suitable solvents precluded the molecular weight determination and growing of a single crystal for X-ray crystallographic studies. Both Pd(II) and Pt(II) complexes are diamagnetic, as would be expected for $d^8$ species, whereas the magnetic moment values from Rh(III) complexes (*ca.* 0.30 BM) correspond to octahedral stereochemistry with a diamagnetic nature. The molar conductances of $10^{-3}$ M solutions of all these compounds in DMF lie below 20 ohm$^{-1}$ cm$^2$ mol$^{-1}$, indicating their non-electrolytic nature. Accordingly, the Pt(II) and Pd(II) complexes can be formulated as $\mathrm{MCl_2}$(DBH) and $\mathrm{MCl_2}$(DClBH) respectively, with three coordination sites of the metal ions being occupied by ligand donors. Rhodium(III), on the other hand, reacts with the aforementioned ligands to afford complexes of the formulae $\mathrm{RhCl_3}$(DBH) and $\mathrm{RhCl_3}$(DClBH), respectively. The ligands here are terdentate as well, affording an octahedral configuration of the central atom, in line with what is known about the chemistry of Rh(III). These formulations have been further corroborated on the basis of spectral properties of these compounds.

The IR spectra of the complexes with their tentative assignments are given in Table II. The ligands are basically substituted pyridine derivatives and extensive IR studies have been made for such compounds [10, 13, 19, 20]. The various pyridine ring vibrations in the free ligands appearing at $\sim$1610–1590, 1650–1580, 1490–1450 and 1440–1435 cm$^{-1}$ are assigned to four $\nu$(C=C) and $\nu$(C=N) vibrations. The other vibrations observed in the spectra of the ligands are at $\sim$990 cm$^{-1}$, a ring breathing mode, at $\sim$800 cm$^{-1}$, an out of plane (C–H) deformation, at $\sim$610 cm$^{-1}$, an inplane (C–C) deformation and at $\sim$410 cm$^{-1}$, an out of plane (C–C) deformation. Furthermore, the strong bands at 795 and 735 cm$^{-1}$ are assigned to $\gamma$(C–H) and $\phi$(C–C), respectively [19, 20]. Moreover, the spectra of the free ligands, apart from the various pyridine ring vibrations, exhibit the usual amide group bands in the regions $\sim$1695, 1515, 1250, 650 and 490 cm$^{-1}$, assignable to amide I, II, III, IV and V, respectively, and suggesting that the ligands exist in the keto-form [21, 22]. However, these ligands are capable of undergoing keto–enol tautomerism and thus can

TABLE II. Relevant IR Frequencies (cm$^{-1}$) of the new Benzoylhydrazone Complexes with their Assignments (KBr discs)[a]

| Compound | $\nu$(N–H) | Amide I $\nu$(C=O) | $\nu$(C=N) | Amide II | $\nu$(N–N) | $\nu$(M–N) | $\nu$(M–O) | $\nu$(M–Cl) |
|---|---|---|---|---|---|---|---|---|
| $\mathrm{PdCl_2}$(DBH) | 3180m, br | 1670vs | 1570m | 1495m | 920s | 450m | 422w | 340s<br>330m |
| $\mathrm{PdCl_2}$(DoClBH) | 3170m, br | 1675vs | 1575m | 1500m | 915s | 445w | 405w | 350m<br>330sh |
| $\mathrm{PdCl_2}$(DmClBH) | 3165m | 1670vs | 1570m | 1500m | 930m | 440m | 410w | 340s<br>320sh |
| $\mathrm{PdCl_2}$(DpClBH) | 3165m | 1675vs | 1580s | 1505w | 935m | 445w | 425w | 340m<br>320w |
| $\mathrm{PtCl_2}$(DBH) | 3170m, br | 1675vs | 1570s | 1500m | 915s | 455w | 418w | 345m<br>330m |
| $\mathrm{PtCl_2}$(DoClBH) | 3160m, br | 1670vs | 1575vs | 1495m | 910m | 465m | 422w | 330m<br>320m |
| $\mathrm{PtCl_2}$(DmClBH) | 3165m, br | 1670vs | 1570s | 1500m | 930m | 460m | 415w | 345m<br>320m |
| $\mathrm{PtCl_2}$(DpClBH) | 3170m | 1675vs | 1580vs | 1490m | 935m | 470m | 410w | 340m<br>320sh |
| $\mathrm{RhCl_3}$(DBH) | 3180m, br | 1655vs | 1565s | 1500w | 930w | 440m | 400w | 330s<br>315w |
| $\mathrm{RhCl_3}$(DoClBH) | 3170m, br | 1660vs | 1570s | 1500w | 925w | 445m | 395m | 325m<br>310w |
| $\mathrm{RhCl_3}$(DmClBH) | 3170m | 1670vs | 1570s | 1500w | 920m | 440w | 400m | 330m<br>310sh |
| $\mathrm{RhCl_3}$(DpClBH) | 3180m, br | 1660vs | 1575s | 1490m | 915m | 445w | 400w | 330m<br>310sh |

[a] vs = very strong, s = strong, m = medium, w = weak, sh = shoulder, br = broad.

coordinate in either of these two forms, depending upon the experimental conditions [17].

In the spectra of the complexes, amide I, amide II and $\nu$(C=N) suffer a negative shift thereby indicating the coordination of the carbonyl oxygen and the nitrogen atom of the azomethine group to the metal ion. Moreover, the band due to $\nu$(N–N) observed at ~900 cm$^{-1}$ in the ligands appears at a higher frequency (~920 cm$^{-1}$) suggesting the involvement of one nitrogen atom of the moiety in coordination, for a shift of more than 30 cm$^{-1}$ is observed in the event of bidentate linkage of the (N–N) group [4]. This is further supported by the position of $\nu$(N–H) which remains unaltered in the spectrum of the complexes, indicating its non-involvement in bonding. Moreover, the spectra of all complexes show considerable changes in pyridine ring vibrations and thus indicate that pyridine nitrogen takes part in coordination in these compounds. Actually, the spectra exhibit a downward shift in $\nu$(C=C) and $\nu$(C=N) vibrations, whereas the 990 cm$^{-1}$ strong band of the ligand, which is assigned to the breathing motion of the pyridine ring, tends to disappear and is replaced by a band at ~1010 cm$^{-1}$ [19, 23]. Furthermore, the band assigned to $\phi$(C–C) splits into two bands at ~720 and 742 cm$^{-1}$, while the $\gamma$(C–H) shows a downward shift and appears at ~785 cm$^{-1}$ as a single band [20]. Finally, the bands at 610 and 410 cm$^{-1}$ show an upward shift of 15–20 cm$^{-1}$ [20, 24]. All these changes suggest the involvement of pyridine nitrogen with the metal atom in the complexes under investigation.

With the aforementioned characteristics of the IR spectra, it can be inferred that the ligands behave as terdentate and coordinate through carbonyl-oxygen, azomethine-nitrogen and pyridine-nitrogen [16, 17]. The tentative structure of the complexes is depicted schematically in Fig. 1.

The terdentate nature of the ligands is further confirmed by far IR spectra, wherein new bands are observed around 440–470 and 405–425 cm$^{-1}$ which can be assigned to $\nu$(M–N) and $\nu$(M–O) vibrations, respectively [25–28]. Furthermore, in the FIR spectra of the studied complexes the medium intensity bands at 345 and 320 cm$^{-1}$ are assigned to the metal–chlorine stretching modes [29–32]. In particular, the FIR spectra of the Pd(II) and Pt(II) complexes show two close bands in the range 350–320 cm$^{-1}$ which have been assigned to asymmetric and symmetric $\nu$(M–Cl) vibrations corresponding to two Cl ligands in *cis*-arrangement [29–31]. In a few cases only one wide band is observed or the long-wave band occurs as a shoulder on the short-wave band. The shoulder could be due to symmetric Pt–Cl vibration and indicates the *cis*-complex. Moreover, when a suspension of PtCl$_2$(DBH) was gently heated with an excess of aqueous pyridine, the solid dissolved gradually to give a pale yellow solution. Addition of solid sodium perchlorate gave white needles of [Pt(py)$_2$(DBH)](ClO$_4$)$_2$. The bands in the FIR spectrum of PtCl$_2$(DBH) which have been assigned to $\nu$(Pt–Cl) vibrations are absent in the spectrum of the product. PtCl$_2$(DClBH) reacts in a similar manner: the chloro groups can be substituted with basic ligands such as pyridine, ammonia or ethylenediamine on mild heating [33].

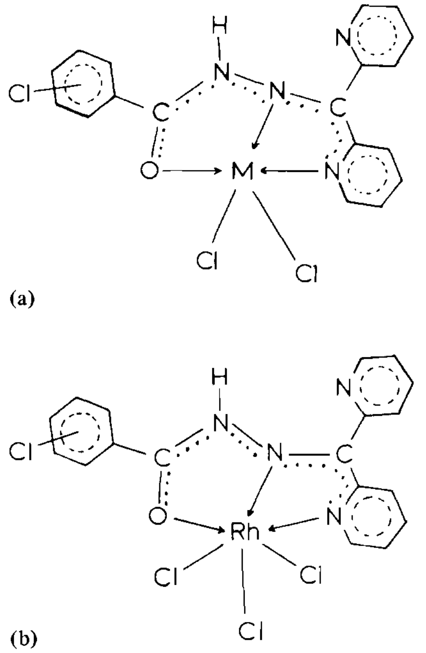

Fig. 1. (a) The proposed geometry for the Pd(II) and Pt(II) chlorobenzoylhydrazone complexes. (b) The tentative structure of the RhCl$_3$(DClBH) complexes.

The electronic spectral data of the complexes (Table III) further support the coordination of the terdentate ligand to the metal through the oxygen and a nitrogen from the hydrazide group and through the pyridine nitrogen. Actually, the ligands exhibit an intense absorption band at ~37.7 kK which shifts to a higher wavelength with increasing solvent polarity and is therefore assigned to a $\pi^* \leftarrow \pi$ transition of the rings [13, 34]. A red shift is also expected for this transition when the N of the pyridine ring is metal coordinated [35]. Spectra obtained in CH$_3$OH solutions show that this occurs in the complexes investigated, implying nitrogen metal coordination in all of them. Another intense absorption band in the region ~36.1 kK in the spectra of the free ligands is attributed to an intraligand transition of the $\pi^* \leftarrow \pi$ type located mainly on the C=N group [13]. This band also occurs in the spectra of the complexes, but is shifted towards higher frequencies, a fact which further supports the idea of the coordination of the hydrazones via the azomethine nitrogen atom. A third intense band in this region appears at ~29.5 kK which undergoes a hypsochromic shift with increasing

TABLE III. Electronic Spectral Data of the new Compounds for DMF Solutions

| Compound | Band I | Band II | Band III | Band IV |
|---|---|---|---|---|
| $\text{PdCl}_2\text{(DBH)}$ | 36.9[a] (3.76)[b] | 30.6 (3.69) | 23.9sh[c] (3.52) | 21.4 (2.32) |
| $\text{PdCl}_2\text{(DoClBH)}$ | 36.5 (4.31) | 30.4sh (3.81) | 24.1 (3.78) | 21.9 (2.05) |
| $\text{PdCl}_2\text{(DmClBH)}$ | 36.7 (4.35) | 30.3sh (3.78) | 23.9sh (3.64) | 21.6 (2.38) |
| $\text{PdCl}_2\text{(DpClBH)}$ | 36.6 (4.13) | 30.5 (3.92) | 23.7sh (3.77) | 21.5 (2.61) |
| $\text{PtCl}_2\text{(DBH)}$ | 36.4 (4.23) | 30.8 (3.87) | 23.5 (3.18) | 21.6 (2.04) |
| $\text{PtCl}_2\text{(DoClBH)}$ | 36.3 (4.19) | 30.9sh (3.75) | 23.9 (3.52) | 21.4 (2.14) |
| $\text{PtCl}_2\text{(DmClBH)}$ | 37.1 (3.97) | 30.7 (3.76) | 23.8 (3.36) | 21.5 (2.12) |
| $\text{PtCl}_2\text{(DpClBH)}$ | 36.8 (4.12) | 30.9sh (3.83) | 24.2 (3.49) | 21.3 (2.06) |
| $\text{RhCl}_3\text{(DBH)}$ | 37.1 (4.33) | 30.8sh (3.77) | 23.7 (3.34) | |
| $\text{RhCl}_3\text{(DoClBH)}$ | 37.0 (3.98) | 30.9sh (3.54) | 23.8 (3.16) | |
| $\text{RhCl}_3\text{(DmClBH)}$ | 36.8 (4.11) | 30.7 (3.72) | 23.7 (3.12) | |
| $\text{RhCl}_3\text{(DpClBH)}$ | 37.3 (4.07) | 30.7 (3.80) | 23.8 (3.15) | |

[a] $\tilde{\nu}$(kK). [b] $\log \epsilon_{\text{mol}}$. [c] sh = shoulder.

solvent polarity. It is therefore assigned to a $\pi^* \leftarrow n$ transition of the carbonyl group. Complex formation through the C=O group should cause a large blue shift of the $\pi^* \leftarrow n$ transition [34, 36]. Actually, in the complexes expected to coordinate the C=O group, this band is shifted by ~1 kK. Finally, the low energy band envelope in the region ~23.5 kK is probably due to a ligand-to-metal charge-transfer transition and is responsible for the colour of these complexes, whereas the band at ~21.5 kK can be assigned as a crystal field band on the basis of its low intensity.

The molecular ions of the studied compounds were not detected in the mass spectra, except in the case of the $\text{RhCl}_3\text{(DpClBH)}$ complex. The absence of molecular ions can be attributed either to pyrolytic decomposition, in the direct inlet, under the high temperature which was used (200–280 °C), or to electron impact. However, in the spectra of Pt(II) and Pd(II) complexes the ion $[\text{(DClBH)}]^{\cdot+}$ was always present and can be regarded as a direct fragment of the molecular ion upon elimination of the metal chloride moiety. Among the most interesting and prominent peaks detected in the high mass region of the spectra of the examined compounds are those corresponding to the ions $[\text{MCl}_2\text{(ClPhC(:O)NHN)}]^+$ and $[\text{MCl}_2\text{(ClPhC:O)}]^+$. These ions may be partly considered to be pyrolytic products, because their relative intensities are affected by the temperature and the time spent in the direct inlet. On the other hand, the molecular ion corresponding to the species $[\text{RhCl}_3\text{(DpClBH)}]^{\cdot+}$ was always observed in the mass spectrum although usually at an intensity of only about 2% of the base peak. This molecular ion showed the characteristic mass distribution expected for the isotopic composition of rhodium. Apart from an *m/e* value corresponding to the formula $[\text{RhCl}_3]^+$ observed in all Rh(III) complexes, the remainder of the mass spectrum consisted of peaks corresponding to the ligand *p*-chlorobenzoyl-di-(2-pyridyl)ketohydrazone and its subsequent fragmentation. That is, $[\text{RhCl}_3\text{(DpClBH)}]^{\cdot+}$ breaks down to $[\text{RhCl}_3]^+$ and $[\text{(DpClBH)}]^{\cdot+}$, with the remaining breakdown pattern being that expected from $[\text{(DpClBH)}]^{\cdot+}$.

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