

CCA-1841

YU ISSN 0011-1643

UDC 541.486

Original Scientific Paper

Pd(II), Pt(II), Rh(III), Ir(III) and Ru(III) Complexes of some Nitrogen-Oxygen Donor Ligands

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Received May 4, 1988

Pd(II), Pt(II), Rh(III), Ir(III) and Ru(III) complexes of propiophenone and butyrophenone semicarbazones (abbreviated PSC and BSC, respectively) have been synthesized and characterized by elemental analysis, magnetic moments and IR and electronic spectral studies. The complexes were found to have the composition of $M(\text{PSC/BSC})_2\text{Cl}_2$ ($M = \text{Pd}$ or Pt) and $M(\text{PSC/BSC})_3\text{Cl}_3$ ($M = \text{Rh}$, Ir and Ru). All the complexes are diamagnetic except $\text{Ru}(\text{PSC/BSC})_3\text{Cl}_3$, which is paramagnetic, Pd(II) and Pt(II) complexes are of square planar geometry. Rh(III), Ru(III) and Ir(III) complexes are six-coordinate octahedral. Various ligand field parameters have been calculated and discussed.

INTRODUCTION

Recently, great interest has arisen in the effect of platinum metal compounds on biological systems. In the literature one can find descriptions of the antibacterial, antiviral and antitumor effect of platinum and palladium compounds.¹⁻⁴ However, professional contact and the use of these compounds as antitumoral preparations often result in a disease known as platinosis,⁵⁻⁷ which is manifested in the form of dermatitis and asthmoid conditions.⁵ These phenomena, at the initial stages, are due to the histamine liberating action of platinum compounds.⁸⁻¹⁰ Investigation of the effect of platinum and palladium compounds on various biological systems, including bacteriophage T-4¹¹⁻¹² and membrane-bound Ca, Mg-dependent AT phase⁷ have shown that the inhibiting activity depends on the degree of oxidation of the metal and on the complex configuration, but the electronic structure of the introduced complexes must be taken into account as well.

There are very few reports¹³⁻¹⁵ on platinum metal complexes of semicarbazones. Keeping this in mind, we have synthesized and characterized the platinum metal complexes of propiophenone and butyrophenone semicarbazones, reported in this paper.

EXPERIMENTAL

(a) Preparation of Ligands

11.15 g (1 mole) semicarbazide hydrochloride (Fluka, A. G., Switzerland) and 10.2 g sodium acetate (AR, BDH, India) were dissolved in 50 ml of double distilled water and 1 mole of propiophenone (13.4 ml, AR grade, E. Merck, W. Germany) or butyrophenone (16.0 ml, AG, Fluka, Switzerland) was added to it. 50 ml alcohol was added to the mixture, the contents was shaken thoroughly and refluxed for about half an hour on a water bath. On cooling, the white coloured semicarbazone separated out. It was filtered off, washed with ethanol and dried over P_4O_{10} .

(b) Preparation of the Complexes

A general method has been used for the preparation of the complexes. A hot aqueous solution (20 ml) of 0.1 mole of the metal chloride of Pt(II), Pd(II), Ru(III), Rh(III) or Ir(III) was mixed with a hot ethanolic solution (20 ml) of 0.2 mole of either semicarbazone. The mixture was refluxed on a water bath for about 2–3 hours. On cooling, the coloured complex precipitated out in each case. The complex was filtered off, washed with 50% aqueous ethanol and dried over P_4O_{10} *in vacuo*.

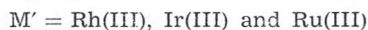
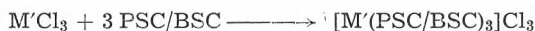
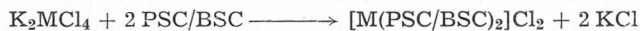
Physical Measurements

Magnetic measurements were carried out using a Princeton Applied Research Model 155 Vibrating Sample magnetometer, incorporating a digital readout. The electromagnet was fed from a Polytronic constant current regulator (type Cp. 200). The current was adjusted so as to produce a magnetic field at 5 kilo gauss. The instrument was calibrated using a standard (analytical) nickel pellet and cross checked against $Hg[Co(CNS)_4]$. IR spectra were recorded on a Perkin Elmer 621 Automatic recording ($4000-400\text{ cm}^{-1}$) spectrophotometer in KBr pellets. Electronic spectra were recorded on a DMR-21 automatic recording spectrophotometer in Nujol mull.

Analyses for carbon and hydrogen were carried out in the microanalytical laboratory of the Department of Chemistry, University of Delhi. Nitrogen was estimated in the Central Drug Research Institute, Lucknow.

RESULTS AND DISCUSSION

The formation of the complexes may be represented by the following reactions:



Elemental analysis reveals that the complexes have the composition $M(\text{PSC/BSC})_2Cl_2$ ($M = \text{Pd or Pt}$) and $M(\text{PSC/BSC})_3Cl_3$ ($M = \text{Ru, Rh and Ir}$) (Table I). Conductivity of these complexes could not be measured due to poor solubility in all common organic solvents.

Palladium(II) and Platinum(II) Complexes

The complexes are diamagnetic as expected for square planar d^8 metal complexes. The electronic spectra of Pd(II) and Pt(II) complexes are indicative of square planar geometry. Three d-d spin allowed transitions are expected corresponding to the transitions^{16,17} from the three lower lying d levels to

TABLE I
Colour, composition and magnetic moment (B. M.) of the complexes/ligands

| Ligand/Complex | Colour | % Yield | m. p. (C) | Elemental Analysis Found (Calcd) | | | | μ_{eff} (B. M.) |
|--------------------------------------|---------------------|---------|------------------|----------------------------------|------------------|----------------|------------------|-------------------------------|
| | | | | %M | %C | %H | %N | |
| PSC | White | 67 | 188 | — | 65.00 (64.39) | 7.88 (7.32) | 21.00 (20.49) | |
| BSC | White | 62 | 174 | — | 63.00 (62.83) | 7.00 (6.81) | 22.40 (21.99) | |
| Pd(PSC) ₂ Cl ₂ | Black | 82 | 158 ^p | 19.00 (19.02) | 42.98 (42.93) | 4.00 (4.65) | 14.68 (15.02) | DM |
| Pt(PSC) ₂ Cl ₂ | Dull white | 90 | 190 | 36.86 (37.03) | 37.00 (37.03) | 4.00 (4.01) | 12.82 (12.95) | DM |
| Ru(PSC) ₃ Cl ₃ | Light yellow | 70 | 120 | 13.66 (13.16) | 30.70 (30.75) | 3.12 (3.33) | 11.00 (10.74) | 1.80 |
| Rh(PSC) ₃ Cl ₃ | Black | 60 | 270 | 13.76 (13.16) | 30.22 (30.67) | 3.42 (3.32) | 10.44 (10.74) | DM |
| Ir(PSC) ₃ Cl ₃ | Light brown | 55 | 310 | 22.00 (22.05) | 28.00 (27.53) | 3.00 (2.96) | 10.22 (9.64) | DM |
| Pd(BSC) ₃ Cl ₃ | Yellow | 75 | 300 | 17.67 (18.11) | 44.90 (44.94) | 4.88 (5.14) | 13.66 (14.30) | DM |
| Pt(BSC) ₂ Cl ₂ | Greenish- yellow | 92 | 170 ^p | 28.00 (28.96) | 39.00 (39.05) | 4.22 (4.44) | 12.00 (12.42) | DM |
| Ru(BSC) ₃ Cl ₃ | Dark brown | 60 | 195 ^p | 11.64 (12.28) | 32.00 (32.07) | 4.00 (3.65) | 10.50 (10.21) | 1.01 |
| Rh(BSC) ₃ Cl ₃ | Light brown | 56 | 245 | 20.63 (21.04) | 32.00 (32.02) | 4.21 (3.64) | 10.80 (10.18) | DM |
| Ir(BSC) ₃ Cl ₃ | Yellow | 55 | 300 | 12.08 (12.70) | 29.22 (28.89) | 4.11 (3.29) | 9.20 (9.19) | DM |

DM = Diamagnetic

D = Decomposed without melting.

the empty $d_{x^2-y^2}$ orbitals; the ground state is $^1A_{1g}$ and excited states corresponding to the above transitions are $^1A_{2g}$, $^1B_{1g}$ and 1E_g in the order of increasing energy. The electronic spectra of the complexes under study display bands at 22,200—24,200 and 29,200—31,000 cm^{-1} (Table II). The first band may be assigned^{16,17} to the $^1A_{1g} \rightarrow ^1B_{1g}$ transition and the second band in the UV region is undoubtedly of charge transfer nature.

TABLE II
Electronic spectral bands (cm^{-1}) and ligand field parameter

| Complex | ν_{max} (cm^{-1}) | $10Dq$ (cm^{-1}) | B (cm^{-1}) | β | C (cm^{-1}) | ν_2/ν_1 | Δ_1 (cm^{-1}) |
|--------------------------------------|--|--------------------------------|-----------------------------|---------|-----------------------------|---------------|------------------------------------|
| Rh(PSC) ₃ Cl ₃ | 17500 20200 24800 | 21550 | 288 | 0.39 | 1350 | 1.15 | — |
| Rh(BSC) ₃ Cl ₃ | 17800 20100 24800 | 21250 | 294 | 0.40 | 1150 | 1.33 | — |
| Ir(PSC) ₃ Cl ₃ | 30800 34000 | 31600 | 200 | 0.33 | 800 | 1.10 | — |
| Ir(BSC) ₃ Cl ₃ | 30800 34200 | 30850 | 212 | 0.32 | 860 | 1.08 | — |
| Ru(PSC) ₃ Cl ₃ | 13650 17600 22700 | 26259 | 494 | 0.78 | 2523 | 1.29 | — |
| Ru(BSC) ₃ Cl ₃ | 13700 17600 22600 | 26054 | 488 | 0.78 | 2479 | 1.28 | — |
| Pd(PSC) ₂ Cl ₂ | 22200 29200 | — | — | — | — | — | 2433 |
| Pd(BSC) ₂ Cl ₂ | 22000 29200 | — | — | — | — | — | 2433 |
| Pt(PSC) ₂ Cl ₂ | 24200 31000 | — | — | — | — | — | 25800 |
| Pt(BSC) ₂ Cl ₂ | 24200 31000 | — | — | — | — | — | 25800 |

By assuming a value of $F_2 - 10F_4 = 600$ for Slater-Codon Interelectronic Repulsion Parameters for both Pd and Pt, it is possible to calculate from the first spin allowed d-d transition¹⁰ the value of Δ_1 (Table II). The splitting parameter increase in the expected order $\text{Pt} > \text{Pd}$.

Rhodium(III) and Iridium(III) Complexes

All the complexes are diamagnetic as expected. This is consistent with an octahedral arrangement of the donor atoms around the metal ion producing a strong field.¹⁹

The electronic spectra of rhodium(III) complexes display bands at 17,500—17,800, 20,100—20,200 and 24,600 cm^{-1} . These spectra resemble those of other six-coordinate rhodium(III) complexes^{16,20-22} and may be assigned to $^1A_{1g} \rightarrow ^3T_{1g}$, $^1A_{1g} \rightarrow ^1T_{1g}$ and $^1A_{1g} \rightarrow ^1T_{2g}$ transitions, in the increasing order of energy. The electronic spectra of d^6 complexes can be used to evaluate²³

ligand field parameters. The values are given in Table II. The values are comparable with those observed for other complexes of this metal ion with nitrogen-oxygen donor ligands.^{20,21-24} The B values are 39–40% of the free ion values, suggesting considerable orbital overlap with strong covalency in the metal ligand σ -bond.

Jorgensen²³ has demonstrated that decreasing the value of β is associated with a reduction in the positive charge of the cation and with the tendency to be reduced to the next lower oxidation state.

The electronic spectra of the iridium(III) complexes display bands in the range of 30,000 and 34,000–34,200 cm^{-1} , which may be assigned²⁴ to ${}^1A_{1g} \rightarrow {}^1T_{1g}$ (ν_1) and ${}^1A_{1g} \rightarrow {}^1T_{2g}$ (ν_2) transitions in the order of increasing energy. The ratio of ν_2/ν_1 in these complexes lies in the range of 1.08–1.10. The two transitions ν_1 and ν_2 have been used to evaluate the ligand field parameters (Table II). The values of these ligand field parameters are comparable with those reported for other iridium(III) complexes involving similar donors.

Ruthenium(III) Complexes

The room temperature magnetic moments of the ruthenium(III) complexes of both ligands lie in the range of 1.80–1.82 B. M. (Table II), which is lower than the predicted value of 2.10 B. M. The lowering in μ_{eff} values may arise either due to lower symmetry ligand fields, metal-metal interactions or extensive electron delocalization.²⁵

The electronic spectra of ruthenium complexes display bands at 13,650–13,700, 17,600 and 22,600–22,700 cm^{-1} , which may be assigned^{16,26-28} to ${}^2T_{2g} \rightarrow {}^2T_{1g}$, ${}^2T_{1g} \rightarrow {}^4T_{2g}$ and ${}^2T_{2g} \rightarrow {}^2A_{2g}$, ${}^2T_{1g}$ transition, in the increasing order of energy. The electronic spectra of these complexes are further rationalized²⁷ in terms of different ligand field parameters (see Table II). The ligand field parameters are comparable with those reported for other ruthenium(III) derivatives involving nitrogen-oxygen donor molecules.^{16,26-28}

IR Spectra of the Complexes

IR spectral bands of the complexes are presented in Tables III and IV. A comparative study of the spectra of the ligands and complexes shows that both semicarbazones behave as bidentate chelating agents as discussed below for all the metal ions, coordinate to the central metal ion through carbonyl oxygen and nitrogen of the $C=N$ group. The position of the ligands in the range of 3500–3000 cm^{-1} remains unaltered in all complexes indicating that there is no coordination through the $N-H$ group. The ligand band at 1670 cm^{-1} due to $C=O$ group, shifts towards the lower side ($\sim 30-60 \text{ cm}^{-1}$) in the complexes, indicating that coordination takes place through oxygen of the $C=O$ group. The $C=N$ ²⁹ in the ligand at 1570 cm^{-1} shifts towards the lower wave number in the IR spectra of the complexes, indicating a lowering of the $C=N$ bond order as a result of metal nitrogen bond formation.³⁰⁻³² The bands in the lower region may be assigned to $M-O$ and $M-N$, respectively.³³⁻³⁴

TABLE III

Selected infrared spectral bands (cm^{-1}) of propiophenone semicarbazone (PSC) and its Pt, Pd, Rh, Ru, Ir metal complexes

| PSC | Pt(PSC) ₂ Cl ₂ | Pd(PSC) ₂ Cl ₂ | Rh(PSC) ₃ Cl ₃ | Ru(PSC) ₃ Cl ₃ | Ir(PSC) ₃ Cl ₃ | Assignment |
|-----------------|--------------------------------------|--------------------------------------|--------------------------------------|--------------------------------------|--------------------------------------|--|
| 3470 | 3470 | 3440 | 3340 | 3440 | 3460 | δNH |
| 3200 | 3450 | | 3180 | | 3090 | |
| (3600— 3100) | 3115 3000 | 3000 | 3000 | 3000 | 3000 | |
| 1670 | 1640 | 1640 | 1640 | 1650 | 1640 | $\nu\text{C}=\text{O}$ |
| 1575 | 1540 | 1510 | 1510 | 1500 | 1540 | $\nu\text{C}=\text{N}$ |
| 1470 | 1480 | | 1490 | | 1470 | νNH_2 |
| 1380 | | | | | 1440 | |
| 1340 | 1340 | 1340 | 1340 | 1300 | | |
| 1295 | 1300 | 1300 | | 1270 | 1300 | $\nu\text{C}-\text{N} + \delta\text{NH}_2$ |
| 700 | 700 | 720 | 710 | | | |
| | 480 | 510 | | 530 | 530 | $\nu\text{M}-\text{O}$ |
| | 410 | 440 | 440 | | 425 | $\nu\text{M}-\text{N}$ |
| | | 410 | 410 | 410 | 410 | |

TABLE IV

Selected infrared spectral bands (cm^{-1}) of butyrophenone-semicarbazone (BSC) and its Pt, Pd, Rh, Ru, and Ir metal complexes

| BSC | Pt(BSC) ₂ Cl ₂ | Pd(BSC) ₂ Cl ₂ | Rh(BSC) ₃ Cl ₃ | Ru(BSC) ₃ Cl ₃ | Ir(BSC) ₃ Cl ₃ | Assignment |
|------|--------------------------------------|--------------------------------------|--------------------------------------|--------------------------------------|--------------------------------------|--|
| 3450 | 3200 | 3240 | 3420— | 3420 | 3400 | δNH |
| 3270 | 3240 | 3240 | 3220 | 3320 | 3220 | |
| 3170 | 3120 | | | 3230 | 3170 | |
| 1670 | 1600 | 1640 | 1630 | 1620 | 1610 | $\nu\text{C}=\text{O}$ |
| 1570 | 1530 | 1510 | 1510 | 1500 | 1510 | $\nu\text{C}=\text{N}$ |
| 1400 | 1400 | | 1400 | 1400 | 1370 | νNH_2 |
| 1375 | | | | | | |
| 1320 | 1300 | 1300 | 1300 | 1300 | 1300 | $\nu\text{C}-\text{N} + \delta\text{NH}_2$ |
| 690 | 644 | 644 | 630 | 505 | 644 | |
| | 510 | 480 | 440 | 450 | 480 | $\nu\text{M}-\text{N}$ |
| | 410 | 422 | 410 | 410 | 410 | $\nu\text{M}-\text{O}$ |

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SAŽETAK

Kompleksi Pd(II), Pt(II), Rh(III), Ir(III) i Ru(III) s ligandima koji sadrže dušik i kisik kao donorske atome

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Opisana je priprava kompleksa Pd(II), Pt(II), Rh(III), Ir(III) i Ru(III) sa semikarbazonima propiofenona i butirofenona (PSC i BSC). Nađeno je, da ti spojevi imaju opću formulu ML_2Cl_2 ($M = Pd, Pt$), odnosno ML_3Cl_3 ($M = Rh, Ir, Ru$; $L = PSC, BSC$). Na osnovi elementnih analiza, elektronskih i infracrvenih spektara, kao i magnetskih mjerenja, za Pd(II) i Pt(II) komplekse predložena je kvadratna struktura, a za Rh(III), Ir(III) i Ru(III) oktaedarska.