Pergamon

Spectrochimica Acta, Vol. 50A, No. 13, pp. 2167–2175, 1994
Copyright © 1994 Elsevier Science Ltd
Printed in Great Britain. All rights reserved
0584–8539(93)E0034–T 0584–8539/94 $7.00 + 0.00

Synthesis and spectral studies of platinum metal complexes of benzoin thiosemicarbazone

OFFIONG E. OFFIONG
Department of Chemistry, University of Calabar, Nigeria

(*Received* 26 *November* 1991; *in final form* 3 *December* 1993; *accepted* 18 *December* 1993)

Abstract—The platinum metal chelates of benzoin thiosemicarbazone obtained with Ru(III), Rh(III), Ir(III), Pd(II) and Pt(II) were prepared from their corresponding halide salts. The complexes were characterized by elemental analysis, conductance measurement, IR, Raman, ^{1}H-NMR, ^{13}C-NMR and UV–visible spectra studies. Various ligand field parameters and nephelauxetic parameters were also calculated. The mode of bonding and the geometry of the ligand environment around the metal ion have been discussed in the light of the available data obtained. Complexes of Ru(III), Rh(III) and Ir(III) are six-coordinate octahedral, while Pd(II) and Pt(II) halide complexes are four-coordinated with halides bridging.

INTRODUCTION

THIOSEMICARBAZONES have received considerable attention in the last few years because of their potential use in pharmacology [1–6] and as analytical reagents [7, 8]. However, there are few reports on platinum metal complexes of thiosemicarbazones [9, 10] despite the enormous pharmacological importance of these metals and their complexes. The present paper deals with the synthesis and the spectra studies of platinum metal complexes with benzoin thiosemicarbazone. The metal complexes were prepared from chlorides of Ru, Rh, Ir and the various halides of Pd(II) and Pt(II).

EXPERIMENTAL

Preparative

The ligand, benzoin thiosemicarbazone (abbreviated as Bn.tsc) was prepared by interacting equimolar amounts of thiosemicarbazide and benzoin dissolved in ethanol, in the presence of a small amount of glacial acetic acid. The ligand was further recrystallized in ethanol, to yield the compound (Fig. 1). The physical properties and analytical data of the compound are given in Table 1, while the selected IR and Raman bands for the ligand are summarized in Table 2.

The metal complexes were prepared by reacting the ligand and the chloride salt of the respective metal in 2:1 ligand:metal salt molar ratio in the cases of Ru(III), Rh(III) and Ir(III) complexes. The complexes were, however, isolated by adjusting the pH of the ethanolic solution to about 6.5 while refluxing. The Pd(II) and Pt(II) complexes were prepared by reacting various halide salts of the metals with the ligand in 1:1 molar ratio at a pH of 9 and then refluxing the resulting solution for about 1 h. The solid chelates were filtered off, washed several times with ethanol and pumped dry.

Physical measurements

The IR spectra in the 4000–200 cm^{-1} region were recorded on KBr disc on a Perkin–Elmer 325 infrared spectrometer. The Raman spectra were obtained with a Cary 83 Raman spectrophotometer with 488.0 nm argon-ion laser excitation. A Perkin–Elmer model 575 spectrophotometer was used to obtain the electronic spectra. ^{1}H-NMR and ^{13}C-NMR spectra of the ligand were recorded with a Jeol 270 MHz spectrometer using TMS as internal standard and are reported as δ. In the δ assignment of protons and carbons, the numbering is given according to that shown in Fig. 1. The carbon, nitrogen and hydrogen content in the compounds were determined using a Perkin–Elmer model 240 analyzer. The amount of palladium in the complexes was determined gravimetrically using dimethylglyoxime as a precipitating agent. Platinum, rhodium, ruthenium and iridium in the complexes were determined by pyrolysis of the solid chelates at 600°C, weighing

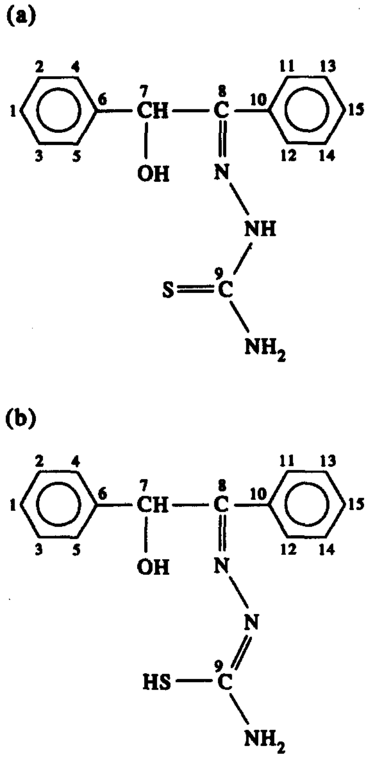


Fig. 1. (a) Thioketo form of benzoin thiosemicarbazone. (b) Thioenol form of benzoin thiosemicarbazone.

the residue obtained as the metal. The halides in the complexes were determined as silver halides, after decomposition of the samples with concentrated nitric/sulphuric acid [11].

Table 1. Physical properties and analytical data of platinum metal complexes of benzoin thiosemicarbazone

Compound	Melting point (°C)	Mol. conductance λ_M(Ohm^{-1} cm^{-2} mol^{-1})	Calculated (%) C	N	H	X	M
Bn.tsc	127	—	63.16 (63.13)	14.61 (14.73)	5.34 (5.30)	—	—
Ru(Bn.tsc)$_2$Cl	300	77.89	50.00 (50.94)	11.93 (11.99)	3.97 (4.00)	5.00 (5.03)	14.30 (14.33)
Rh(Bn.tsc)$_2$Cl	160	72.56	49.31 (50.81)	11.61 (11.84)	3.96 (3.99)	4.96 (5.01)	14.49 (14.53)
Ir(Bn.tsc)$_2$Cl	253	69.00	35.20 (35.12)	8.28 (8.19)	2.99 (2.95)	7.10 (6.91)	37.60 (37.47)
Pd(Bn.tsc)Cl	180	5.91	42.30 (42.11)	9.89 (9.84)	3.36 (3.31)	8.25 (8.31)	24.90 (24.95)
Pd(Bn.tsc)Br	188	5.10	38.12 (38.20)	8.96 (8.90)	3.15 (3.20)	16.60 (16.94)	22.42 (22.56)
Pd(Bn.tsc)I	155	5.06	34.63 (34.74)	8.03 (8.10)	2.90 (2.92)	24.10 (24.46)	20.01 (20.51)
Pt(Bn.tsc)Cl	300	5.88	34.90 (34.92)	8.14 (8.15)	2.70 (2.74)	6.75 (6.80)	37.70 (37.70)
Pt(Bn.tsc)Br	283	5.71	32.03 (32.15)	7.42 (7.50)	2.63 (2.70)	14.11 (14.26)	34.99 (34.81)
Pt(Bn.tsc)I	245	5.00	29.75 (29.66)	6.97 (6.92)	2.55 (2.49)	19.99 (20.89)	34.05 (32.12)

Table 2. Selected IR and Raman (in parentheses) bands for the benzoin thiosemicarbazone and its metal complexes (cm^{-1})

Compound	ν_{OH}	ν_a(NH)	ν_s(NH)	δ(NH)	ν(C=N)	ν(CN) + δ(NH)	ν(CN) + ν(N–N)	ν(C=S)	νM–O	νM–N	νM–S	νM–X
Bn.tsc	3420 s	3260 s	3160 s	1603 sh (1621) (1579)	1615 vs (1600)	1500 m (1511)	1120 m (1069)	900 s (890) (720)				
Ru(Bn.tsc)$_2$Cl	—	3261 s	3166 s	1605 s (1623) (1583)	1603 s (1595)	1520 m (1506)	1111 m (1071)	840 m (888) (717)	540 m	485 m	365 m	—
Rh(Bn.tsc)$_2$Cl	—	3263 s	3160 s	1604 sh (1623) (1580)	1600 s (1591)	1524 m (1510)	— (1073)	835 m (872) (715)	515 m	470 m	350 m	—
Ir(Bn.tsc)$_2$Cl	—	3257 m	3162 s	1600 m (1620) (1579)	1595 s (1587)	1525 m —	1125 m (1079)	834 m (875) (717)	502 m	455 m	333 m	—
Pd(Bn.tsc)Cl	—	3265 s	3170 s	1605 s (1625) (1572)	1600 m —	1528 (1513)	1123 (1083)	898 (889) (718)	520 m	475 m	—	325 m
Pd(Bn.tsc)Br	—	3253 s	3155 s	1591 m (1620) (1570)	1595 m (1581)	1525 m —	1112 (1082)	900 m (890) (718)	519 m	470 m	—	240 m
Pd(Bn.tsc)I	—	3232 m	3144 m	1569 m (1620) (1567)	1589 m (1518)	—	1100 m	900 w (890) (717)	499 w	—	—	205 m
Pt(Bn.tsc)Cl	—	3266 s	3173 s	1600 sh (1618) (1563)	1600 m (1580)	1525 m (1510)	1116 m (1079)	902 s (891) (719)	480 m	465 m	—	285 m
Pt(Bn.tsc)Br	—	3260 s	3153 m	1560 w (1614) (1563)	1590 w —	—	1111 m (1079)	899 m (890) (720)	472 m	440 m	—	210 m
Pt(Bn.tsc)I	—	3230 m	3140 w	1555 w (1609)	— (1570)	—	—	— (890) (718)	450	425	—	180 w

RESULTS AND DISCUSSION

The elemental analysis results support the stoichiometry of the solid chelates as 1:2 metal–ligand ratio for Ru(III), Rh(III) and Ir(III) complexes, while 1:1 metal–ligand ratios were found in the cases of Pd(II) and Pt(II) complexes. The ligand and its complexes are air stable. However, the complexes are slightly soluble in common organic solvents, and very soluble in DMSO and DMF. The Pd(II) and Pt(II) complexes are non-electrolytes, whereas the conductivity data (Table 1) for Ru(III), Rh(III) and Ir(III) suggest a 1:1 electrolytic behaviour in DMF solution.

Infrared spectra

The main infrared bands of benzoin thiosemicarbazone as well as those of the metal complexes in the whole 4000–200 cm^{-1} region are given in Table 2, along with their tentative assignments. The tentative assignments in typical cases are based on the previous work done. However, the IR spectra of benzoin thiosemicarbazone complexes have been extensively used as indicative for the coordination modes of the ligands. In general, the spectra show a large number of bands, most of them generated by aromatic and aliphatic substituents. It is not an easy task to extract bands resulting mainly from the thiosemicarbazide moiety of the ligand. These bands are probably strongly coupled to former vibrations and it is far from accurate to describe them as pure modes, e.g. as ν(C=N) vibration. No bands are observed near the 2500 cm^{-1} assignable to the SH group vibrations [12] which supports the theory that these are the thione form of the thiosemicarbazone used. This is also revealed by the appearance of an intense νC=S band at 900 cm^{-1} further supporting the idea that the ligand is in thione form (Fig. 1a), at least in the solid state. However, in solution it is likely that the thione form exists in equilibrium with the thioenol tautometric form (Fig. 1b). The νC=S vibration band appeared at a lower wavenumber in the spectra of some complexes. This suggests the coordination of the ligand to metal through the sulphur atom of C=S. The band at 3420 cm^{-1} assigned to the ν_{OH} vibration mode in the free ligand, disappeared in the IR spectra of the complexes, indicative of the deprotonation of the hydroxyl group upon coordination to the metal [13, 14]. The band at 1615 cm^{-1}, assigned to νC=N vibration mode in the free ligand, shifts to a higher wave number (~10–15 cm^{-1}). Similar observations had earlier been reported [15, 16], attributed to a positive involvement of the C=N group. A combination band involving νCN + νN–N vibrating mode is assigned to the medium intensity band at 1120 cm^{-1}. This band is slightly affected by complex formation, due to the elongation of the N–N bond and a charge localization on the C=N bond. Another probable combination band is assigned to a medium intensity band at 1500 cm^{-1} attributed to ν(CN) + δ(NH) vibration coupling mode. This band shifts to 1520–1530 cm^{-1} in the metal complexes. This further supports the coordination of the ligand to the metal through the nitrogen of the (C=N–) azomethine group.

Far IR spectra

Table 2 also gives far IR spectra data and their proposed tentative assignments. The bands between 520 and 450 cm^{-1} in the spectra of the complexes which are absent in the spectrum of the ligand are assigned to metal–oxygen, ν(M–O), vibration [17, 18]. The metal–nitrogen vibration, νM–N, bands are assigned to the new bands in the spectra of the complexes between 485 and 425 cm^{-1} [19], while the far IR region between 370 and 320 cm^{-1} gives the metal–sulphur band stretching [20]. However, the νM–S vibrational mode seems to be coupling with the ring deformation mode [21]. The metal–halide vibrations have been studied by comparing the various halide complexes of Pt(II) and Pd(II). The band at 325 cm^{-1} is assigned to the νPd–Cl vibrational mode, while νPd–Br is observed at 240 cm^{-1}. The ratio ν(Pt–Br)/ν(Pd–Br)/ν(Pd–Cl) ≈ 0.74 and that of ν(Pd–I)/ν(Pd–Cl) ≈ 0.63 are in line with the expected four coordination configurations [22]. Similarly the band at 285 cm^{-1} is assigned to Pt–Cl vibration, while Pt–Br and Pt–I

Table 3. ^{1}H NMR Chemical shift δ(ppm) of benzoin thiosemicarbazone and its complexes

Compound	2′NH	4′NH$_2$	OH	Ph–CH	m, 2H, Ar	m, 2H, Ar	m, 4H, Ar	m, 2H, Ar
Bn.tsc	12.30	11.46 (s) 11.21 (s)	9.80 (s)	4.85 (s)	7.90	7.70	7.60	7.39
Pd(Bn.tsc)Cl		11.42 (s)	—	4.43 (s)	7.65	7.60	7.46	7.31
Pd(Bn.tsc)Br	12.00 (br)	11.41 (s)	—	4.43 (s)	7.65	7.61	7.44	7.32
Pd(Bn.tsc)I		11.41 (s)	—	4.45 (s)	7.65	7.60	7.43	7.32
Pt(Bn.tsc)Cl		11.39 (s)	—	4.46 (s)	7.64	7.57	7.41	7.33
Pt(Bn.tsc)Br		11.39 (s)	—	4.46 (s)	7.63	7.59	7.41	7.34
Pt(Bn.tsc)I	12.00 (br)	11.38 (s)	—	4.45 (s)	7.64	7.59	7.42	7.34

m = multiplet, br = broad, s = singlet.

are found at 210 and 184 cm^{-1}, respectively. The ratio ν(Pt–Br)/ν(Pt–Cl) ≈ 0.74 and ν(Pt–I)/ν(Pt–Cl) ≈ 0.63 are expected values for four-coordinated complexes.

Raman spectra

Table 2 reports Raman spectral data and their tentative assignments (in parentheses). The ligands exhibit two intense bands in the region of 1600–1621 cm^{-1} and 1511 cm^{-1}. These bands shift to higher energy or lower energy in complexes. They are considered to have sufficient contributions from ν(C=N) vibration and the change in energy indicates coordination through azomethine nitrogen. The Raman band in the region 870–890 cm^{-1} could be assigned to ν(C=S). This band is split into two maxima having lower energies and appears in the region of 717–720 cm^{-1} which could be assigned to ν(C–S) vibration. The band at 320–380 cm^{-1} probably results from the ν(M–S) vibration.

^{1}H-*NMR spectra*

The proton magnetic resonance spectra of benzoin thiosemicarbazone and its complexes have been recorded in DMSO-d$_6$ using TMS as the internal standard. The chemical shift values (δ, ppm) of the different protons have been recorded in Table 3. The spectra of the thiosemicarbazone exhibit two resonances for the $^{4}NH_2$ protons, indicating hindered rotation about C(s)–$^{4}NH_2$ bond due to its partial double bond character [23, 24]. The ^{1}H-NMR spectra of thiosemicarbazone also exhibit a sharp singlet due to the ^{2}NH group in the region of δ 12.3. This signal disappears on metal chelation in most cases, or broadens and diminishes in intensity in a few cases. The broad band at δ 9.80 is assigned to an OH proton. This band disappears in the spectra of the complexes, suggesting deprotonation of the OH group upon coordination to the metal ion. The signal at δ 4.85 in the ligand is attributed to a benzylic proton, this undergoes deshielding to a magnitude of 0.45 ppm in the complexes, supporting the involvement of the OH group in the bond formation.

^{13}C-*NMR spectra*

The ^{13}C-NMR spectra of benzoin thiosemicarbazone and its metal complexes are represented in Table 4. The carbon resonance assignment for $^{9}C{=}S$, $^{8}C{=}N$ and $^{7}CH{-}OH$

Table 4. ^{13}C NMR Chemical shift (ppm) of benzoin thiosemicarbazone and its complexes

Compound	C-1	C-2/C-3	C-4/C-5	C-6	C-7	C-8	C-9	C-10	C-11/C-12	C-13/C-14	C-15
Bn.tsc	134.1	126.7	127.1	131.0	140.0	145.0	158.9	133.3	129.6	129.4	130.5
Pd(Bn.tsc)Cl	131.8	124.8	126.8	131.39	150.6	125.4	158.8	132.7	129.3	126.69	128.4
Pd(Bn.tsc)Br	131.2	124.0	125.8	131.35	150.1	125.0	158.8	132.3	129.2	126.69	128.0
Pd(Bn.tsc)I	131.1	124.0	125.7	131.33	150.1	125.1	158.8	132.1	129.1	126.66	128.0
Pt(Bn.tsc)Cl	131.1	124.1	125.7	131.3	149.9	125.1	158.6	132.0	129.1	126.53	128.0
Pt(Bn.tsc)Br	130.9	123.8	125.7	131.3	149.7	125.0	158.5	132.0	129.1	126.50	127.8
Pt(Bn.tsc)I	130.7	123.5	125.6	131.2	149.6	125.0	158.4	131.9	129.0	126.50	127.6

are in agreement with those reported in the literature [23–25]. The carbon-13 NMR chemical shifts are more informative, definitive and conclusive. In all the Pt(II) and Pd(II) complexes, upfield chemical shifts are observed for all the carbon resonances adjacent to the assumed coordination sites, except the ^{9}C=S carbon, which like the rest is slightly affected or remains essentially unchanged. The most upfield shifted carbon resonances are C-7 and C-8, which were shifted relative to the free ligand by about 10.0 and 20.0 ppm, respectively. These large chemical shifts are in support of coordination via hydroxyl group and azomethine nitrogen. Since the signal due to C=S appears to remain essentially unchanged, this suggests the non-participation of the C=S group in the bond formation with metal ions. This further suggests that the ligand is present as a monobasic bidentate molecule in the Pt(II) and Pd(II) complexes.

Electronic spectra

The electronic spectra data of the metal complexes were recorded in DMF solution. The positions of the absorption bands obtained were not significantly different from those in the solid state diffuse reflectance spectra, suggesting no electronic or geometric change of the species in dissolution in DMF.

The electronic spectrum of Ru(Bn.tsc)$_2$Cl complex gave band with λ_{max} at 17,500, 21,900 and 24,800 cm^{-1}. The first and third bands have been assigned to the spin-forbidden transitions [26]

$$^2T_{1g}\rightarrow{}^2E_g \text{ and } {}^2T_{1g}\rightarrow{}^2A_{1g}.$$

The separation energy between these two transitions corresponds to 8B [27] and the value of the crystal field splitting energy (10 Dq) has therefore been calculated from the ratio Dq/B = 5.1. The band at 21,900 cm^{-1} is spin-allowed transition $^2T_{2g}\rightarrow{}^2A_{2g}$ of the Ru(III) complex in octahedral field. The ligand field parameters (Table 5) are consistent with an inner-orbital low-spin distorted stereochemistry of the ligand around Ru(III) ion. The rhodium complex, Rh(Bn.tsc)$_2$Cl gives absorption bands, having λ_{max} at 16,880 and 28,570 cm^{-1}, which has accordingly been assigned to $^1A_{1g}\rightarrow{}^1T_{ig}$ and $^1A_{1g}\rightarrow{}^1T_{2g}$ transitions respectively. The third weak intensity band at 39,210 cm^{-1} assigned to charge transfer transition $^1A_{1g}\rightarrow b$, $^1T_{1u}$. Using Eqns (1) and (2) below, the ligand field parameters (10 Dq, B, β and LFSE) have been calculated (Table 5):

$$\nu_1 = 10\,\text{Dq} - 4B + 86(B)^2/10\,\text{Dq} \qquad (1)$$

$$\nu_2 = 10\,\text{Dq} + 12B + 2(B)^2/10\,\text{Dq}. \qquad (2)$$

The B value obtained for the Rh(Bn.tsc)$_2$Cl complex is of the order of 57% of the corresponding free ion value (720 cm^{-1}) suggesting a considerable orbital overlap with a strong covalency in the metal–ligand sigma bond. The reduced value of B may also be associated with the reduction in the effective cationic charge (z^*). The UV–visible solution spectra of Ir(III) with benzoin thiosemicarbazone (Bn.tsc) may also involve intra-ligand, charge transfer and *d-d* transitions which are found at decreasing energy and intensity. The visible absorption spectra of Ir(III) complex may be expected to consist of transition from the $^1A_{1g}$ ground state to other singlet state similar to the Rh(III) complex. Although the entire energy level pattern for Ir(III) is not well known or documented in full detail, the two absorption bands at 18,690 and 28,570 cm^{-1}, found in the spectrum of Ir(Bn.tsc)$_2$Cl, may represent transitions to the upper state $^1T_{1g}$ and $^1T_{2g}$. Thus, the inherent tendency of the octahedral d^6 configuration to adopt the low-spin t_{2g}^2 arrangement, together with the relatively high ligand field strengths in these complexes of tripositive higher transition series ions, as well as the fact of the $5d^6$ or $3d^6$ ones, provide a combination of factors that evidently leaves no possibility of there being any high-spin octahedral complex of Ir(III) with benzoin thiosemicarbazone. This is further

Table 5. Electronic spectral bands and ligand field parameters

Complex	Bands (cm^{-1})	Assignments	10 Dq	*B*	β	LFSE (cm^{-1})
Ru(Bn.tsc)Cl	12,500	${}^2T_{1g}$—${}^2E_g$	46,512	912		16,482
	21,900	${}^2T_{2g}$—${}^2A_{2g}$				
	24,800	${}^2T_{1g}$—${}^2A_{1g}$				
Rh(Bn.tsc)$_2$Cl	16,880	${}^1A_{1g}$—${}^1T_{1g}$	24,528	412	0.57	10,404
	28,570	${}^1A_{1g}$—${}^1T_{2g}$				
	39,210	${}^1A_{1g}$—b, ${}^1T_{1u}$				
Ir(Bn.tsc)$_2$Cl	18,690	${}^1A_{1g}$—${}^1T_{1g}$	24,632	365	0.55	11,865
	28,570	${}^1A_{1g}$—${}^1T_{2g}$				
	43,950	${}^1A_{1g}$—b, ${}^1T_{1u}$				
Pd(Bn.tsc)Cl	19,800	${}^1A_{1g}$—${}^1A_{2g}$	—	—	—	—
	21,900	${}^1A_{1g}$—${}^1B_{1g}$				
	26,000	${}^1A_{1g}$—${}^1E_g$				
Pd(Bn.tsc)Br	20,000	${}^1A_{1g}$—${}^1A_{2g}$	—	—	—	—
	23,100	${}^1A_{1g}$—${}^1B_{1g}$				
	26,500	${}^1A_{1g}$—${}^1E_g$				
Pd(Bn.tsc)I	16,800	${}^1A_{1g}$—${}^1A_{2g}$	—	—	—	—
	17,500	${}^1A_{1g}$—${}^1B_{1g}$				
	21,000	${}^1A_{1g}$—${}^1E_g$				
Pt(Bn.tsc)Cl	18,800	${}^1A_{1g}$—${}^1A_{2g}$	—	—	—	—
	21,800	${}^1A_{1g}$—${}^1B_{1g}$				
	26,000	${}^1A_{1g}$—${}^1E_g$				
Pt(Bn.tsc)Br	19,000	${}^1A_{1g}$—${}^1A_{2g}$	—	—	—	—
	21,000	${}^1A_{1g}$—${}^1B_{1g}$				
	26,100	${}^1A_{1g}$—${}^1E_g$				
Pt(Bn.tsc)I	15,300	${}^1A_{1g}$—${}^1A_{2g}$	—	—	—	—
	16,600	${}^1A_{1g}$—${}^1B_{1g}$				
	20,000	${}^1A_{1g}$—${}^1E_g$				

supported by the large 10 Dq value of 24,360 cm^{-1}. A general structure (Fig. 3) is proposed for the Rh(III), Ru(III) and Ir(III) benzoin thiosemicarbazone complexes.

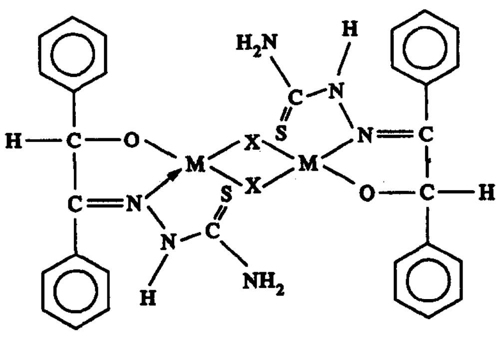
Table 5 reports the electronic spectra for the Pd(II) and Pt(II) complexes. The bands of the absorption spectra for Pd(II) complexes with λ_{max} at 16,800–20,000, 17,500–23,100 and 21,000–26,500 cm^{-1} ranges may be assigned to spin-allowed *d–d* type transitions, corresponding to the one electron transitions

$$b_{2g}(\pi^{\ddagger}) \rightarrow b_{1g}(\delta^{\ddagger})({}^1A_{1g} \rightarrow {}^1A_{2g})$$

$$a_{1g}(\delta^{\ddagger}) \rightarrow b_{1g}(\delta^{\ddagger})({}^1A_{1g} \rightarrow {}^1B_{1g})$$

and, e.g.

$$(\pi^{\ddagger}) \rightarrow b_{1g}(\delta^{\ddagger})({}^1A_{1g} \rightarrow {}^1E_g).$$

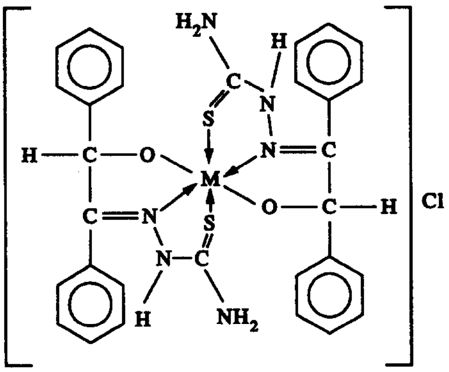


M = Pd (II) or Pt (II)
X = Cl^-, Br^- or I^-

Fig. 2. Platinum and palladium complexes of benzoin thiosemicarbazone.

Table 6. Single electron parameters (cm^{-1})

Complex	Δ_1	Δ_2	Δ_3
Pd(Bn.tsc)Cl	21,150	11,530	1743
Pd(Bn.tsc)Br	21,350	12,530	1043
Pd(Bn.tsc)I	18,150	10,130	1143
Pt(Bn.tsc)Cl	20,150	12,430	1843
Pt(Bn.tsc)Br	21,350	12,530	1043
Pt(Bn.tsc)I	18,150	10,130	1143



M = Rh (III), Ru (III) or Ir (III)

Fig. 3. Octahedral complexes of benzoin thiosemicarbazone.

Similarly, Pt(II) complexes displayed absorption spectra with λ_{max} at 15,300–19,000, 16,600–21,800 and 20,000–26,100 cm^{-1} ranges, attributed to the above transitions. The values of various single electron parameters Δ_1, Δ_2, and Δ_3 have been calculated (Table 6) and they are comparable to those observed for other platinum complexes involving similar donor atoms [9], with square planar geometry. The square planar stereochemistry could be depicted as shown in Fig. 2, for Pt(II) and Pd(II) complexes, involving halides as bridging atoms. The presence of halides as bridging atoms is supported by the relatively lower values of the νM–X vibration mode in Table 2.

In the UV region, there were strong absorptions above 30,000 cm^{-1}; these may be due to charge-transfer bands.

Acknowledgements—The author wishes to gratefully acknowledge the Grant-in-Aid of Research from Sigma Xi, the Scientific Research Society, U.S.A. The work was also supported by Senate Research Grants, University of Calabar, Nigeria.

REFERENCES

[1] C. J. Pfan, *Handbook of Experimental Pharmacology* (*Chemother. Viral Infect.*) **61**, 147 (1982).
[2] A. C. Sartorelli, Cancer chemotherapy, *ACS Symp. Ser. 30*, Washington, D.C. (1976).
[3] A. S. Dobeck, D. L. Klayman, E. T. Dickson, J. P. Scovil and C. N. Oster, *Arzneim. Forsch/Drug Res.* **33**, 1583 (1983).
[4] S. Padhye and G. B. Kauffman, *Coord. Chem. Rev.* **63**, 127 (1985).
[5] R. W. Byrnes, M. Mohan, W. E. Antholine, R. X. Xy and D. H. Petering, *Biochemistry* **29**, 7046 (1990).
[6] Z. Xu, E. C. Alyea, G. Ferguson and M. C. Jennings, *Polyhedron* **10**, 1625 (1991).
[7] R. B. Singh, B. S. Garg and R. P. Singh, *Talanta* **25**, 619 (1978).
[8] A. G. Asuero and M. Gonzalez-Balairon, *Microchem. J.* **25**, 14 (1980).
[9] S. K. Sahni, P. C. Jain and V. B. Rana, *India J. Chem.* **18A**, 161 (1979).
[10] M. M. Patel and M. R. Patel, *J. Indian Chem. Soc.* **57**, 748 (1980).
[11] V. M. Leovac, V. T. Ceslevic and N. Galesic, *Polyhedron* **7**, 2641 (1988).

[12] M. Ferrai Belicchi, G. Fava Gasparri, E. Leporati, C. Pelizzi, P. Tarasconi and G. Tosi, *J. Chem. Soc. Dalton Trans.* 2455 (1986).

[13] M. C. Jain, R. K. Sharma, A. K. Srivastava and P. C. Jain, *J. Inorg. Nucl. Chem.* **41**, 305 (1979).

[14] L. D. Dave and S. K. Thampy, *J. Indian Chem. Soc.* **58**, 538 (1981).

[15] R. C. Aggarwal, T. Prasad and B. N. Yadau, *J. Inorg. Nucl. Chem.* **37**, 899 (1975).

[16] V. J. Babar, D. V. Khasmis and V. M. Shinde, *J. Indian Chem. Soc.* **58**, 970 (1981).

[17] R. C. Aggarwal and T. R. Rao, *J. Inorg. Nucl. Chem.* **40**, 171 (1978).

[18] J. R. Ferraro, *Low Frequency Vibration of Inorganic and Coordination Compounds*. Plenum Press, New York (1971).

[19] J. R. Durig, R. Layton, D. W. Sink and B. R. Mitchell, *Spectrochim. Acta* **21**, 1367 (1965).

[20] B. B. Kaul and K. B. Pandeya, *J. Inorg. Nucl. Chem.* **40**, 1035 (1977).

[21] A. C. Fabretti, A. Giusti, C. Preti, G. Tosi and P. Zannini, *Polyhedron* **5**, 871 (1986).

[22] R. J. H. Clark and C. S. Williams, *Inorg. Chem.* **4**, 350 (1965).

[23] S. Monogaran and D. M. Sathyanarayana, *J. Molec. Struct.* **96**, 73 (1982).

[24] P. Umapathy, A. P. Bhudhkar and C. S. Dorai, *J. Indian Chem. Soc.* **63**, 741.

[25] K. R. Koch, *Inorg. Chim. Acta* **147**, 227 (1988).

[26] R. C. Saxena, C. L. Jain, R. Benjamin and S. K. Sangal, *J. Indian Chem. Soc.* **63**, 435 (1986).

[27] Y. Thakur and B. N. Jha, *J. Inorg. Nucl. Chem.* **42**, 449 (1980).

[28] V. B. Rana, P. C. Jain, M. P. Swami and A. K. Srivastava, *J. Inorg. Nucl. Chem.* **37**, 1824 (1975).