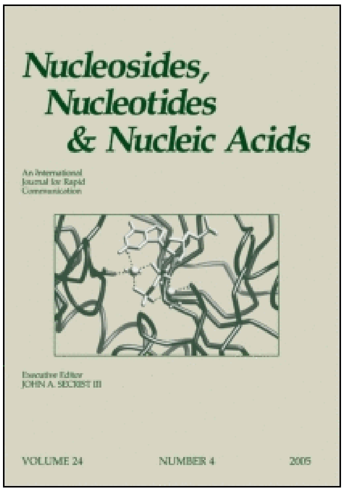

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Complexing Properties of Some Pyrimidines

Mamdouh S. Masoud[a]; Sawsan S. Haggag[a]; Ekram A. Khalil[a]
[a] Chemistry Department, Faculty of Science, Alexandria University, Alexandria, Egypt

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COMPLEXING PROPERTIES OF SOME PYRIMIDINES

Mamdouh S. Masoud, Sawsan S. Haggag, and Ekram A. Khalil
□ *Chemistry Department, Faculty of Science, Alexandria University, Alexandria, Egypt*

□ *The synthesis of transition metal barbiturate, and thiobarbiturate complexes containing different functional groups of variable electronic character with* Co^{II}, Ni^{II}, Cu^{II}, Pd^{II}, *and* Pt^{II} *have been prepared. The stereochemistry and the mode of bonding of the complexes were determined by elemental analysis and electronic and vibrational spectra together with their magnetic moment values. Electronic spin resonance of copper complexes were recorded. The Racah parameter of some cobalt and nickel complexes were calculated. Some of the complexes are of mixed stereochemistry. All the* Pd^{II} *or* Pt^{II} *complexes are of square planar geometries.*

INTRODUCTION

Pyrimidines are one of the most important compounds due to their biological activity and are involved in the structure of nucleic acid in living systems.[1,2] The nucleic acid is related to antimetabolites used in anticarcinogenic chemotherapy.[3] Compounds containing nitrogen and sulphur as donor atoms have an important role to play as anticancer and antiviral agents.[4,5] Barbiturates are used as hypnotic drugs and produce depressive effect on the central nervous system.[6] The metal ions involved with pyrimidine nucleus-lead to an understanding of the complex biological processes occurring in living systems. In our laboratory, studies were reported on the structural chemistry of pyrimidine compounds and the transition metal complexes.[7–17] The structural chemistry of organic ligands (Figures 1 and 2) and their transition metal complexes are the aims of this manuscript. The scope of this investigation includes the characterization of the synthesized multidentate ligands, and their cobalt, nickel, copper, palladium, and platinum through elemental analysis, spectral (UV-Vis, IR and ESR), Racah parameter of (cobalt and nickel) complexes, and magnetic susceptibility measurements.

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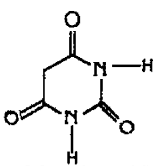
Address correspondence to Mamdouh S. Masoud, Chemistry Department, Faculty of Science, Alexandria University, Alexandria, Egypt. E-mail:

EXPERIMENTAL

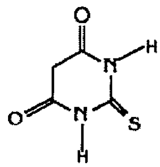
Synthesis of Organic Compounds

The azo compounds (1) were prepared using the usual diazotization process.[8] (X: -H, -NO_2, -Cl, -COOH, -$CH_{[3]}$, -OH). 5-(3-Aldehydo phenylazo) thiobarbituric compound was treated with hydroxylamine hydrochloride at room temperature, in the mole ratio (1:1) to obtain 5-(3-aldoxime arylazo) thiobarbituric acid (X: = NOH). The condensed products (2) were prepared by refluxing the corresponding acids [(BA) or (SBA)] with the desired aldehyde (benzaldehyde and salicylaldehyde) dissolved in 30 mL dioxane. The obtained compounds were filtered off, crystallized from ethanol, then dried in a vacuum desiccator over P_4O_{10}. Their analytical data are collected in Table 1.

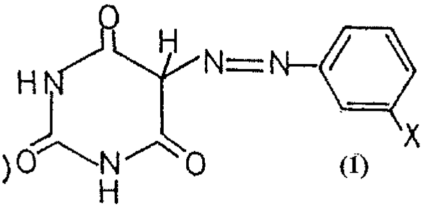
A general skeleton for the prepared compound is given as follows:



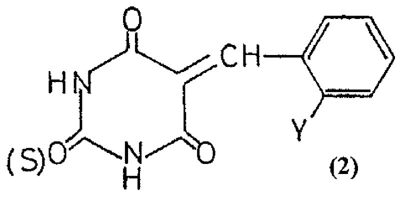
barbituric acid



thiobarbituric acid



(1)



(2)

X = -H	5-(arylazo)barbituric -H(BA)	acid	Y = -H 5-(3-benzilidence) barbituric acid -Bzd (BA)
X = -NO_2	5-(3-nitroarylazo)barbituric -NO_2 (BA)	acid	Y = -H 5-(3-benzilidine) thiobarbituric acid -Bzd (SBA)
X = -Cl	5-(3-chloroarylazo)barbituric -Cl(BA)	acid	Y = -OH 5-(3-salicylidine) barbituric acid -Sal (BA)
X = -COOH	5-(3-carboxyarylazo)barbituric -COOH(BA)	acid	Y = -OH 5-(3-salicylidine) thiolarbituric acid -Sal (SBA)

X = -CHO 5-(3-aldehydoarylazo)barbituric acid
CHO(BA)
X = -CH_3 5-(-3-tolyarylyazo)barbituric acid
-CH_3(BA) X = -OH 5-(-3-hydoroxyarlyazo)barbituric acid
-OH(BA) X = (=NOH) 5-(3-aldoximarylazo)thiobarbituric acid
= NOH(SBA)

-BA	= barbituric acid	-SBA	= thiobarbituric acid
-Bzd	= benzilidine	-Sal	= salicylidene

TABLE 1 Analytical Data for Ligands and Its Metal Complexes, Nujol Mull Electronic Spectra (cm^{-1}) and Magnetic Susceptibility

				% Found (% calculated)[a]				
Compound	Color	Formula	Stoichiometry	C	H	N	M	
Pd-[BA]	Green	$Pd.C_{16}H_{12}N_8O_{12}$	1:4	31.5 (31.3)	2.2 (1.9)	18.5 (18.2)	17.2 (17.3)	28,902
Pt-[BA]	Yellow	$Pt.C_8H_6N_4O_6$	1:2	21.5 (21.4)	1.6 (1.3)	12.5 (12.5)		29,240
Pd-[SBA]	Brown	$Pd.C_{16}H_{20}N_8O_{12}S_4$	1:4 $4H_2O$	25.8 (25.5)	2.9 (2.7)	15.2 (14.9)	13.6 (14.1)	29,940
Pt-[SBA]	Buff	$Pt.C_8H_6N_4O_4S_2$	1:2	20.7 (19.9)	1.5 (1.2)	12.1 (11.6)		29,240
-H[BA]	Yellow	$C_{10}H_8N_4O_3$		51.6 (51.7)	3.3 (3.4)	24.2 (24.1)		
Pd-H[BA]	Dark brown	$Pd.C_{10}H_7N_4O_3$	1:1	35.8 (35.6)	2.5 (2.1)	16.8 (16.6)	32.1 (31.5)	26,455
Pt-H[BA]	Yellow	$Pt.C_{20}H_{28}N_8O_{13}$	1:2 $7H_2O$	30.0 (30.6)	3.2 (3.5)	14.0 (14.3)		24,390
-NO_2[BA]	Yellow	$C_{10}H_7N_5O_5$		43.0 (43.3)	2.2 (2.5)	25.0 (25.2)		
Co-NO_2[BA]	Brown	$Co.C_{10}H_{22}N_5O_{13}$	1:1 8 H_2O	25.3 (25.1)	4.5 (4.6)	14.9 (14.6)	12.1 (12.3)	23,041
Ni-NO_2[BA]	Brown	$Ni.C_{10}H_8N_5O_6$	1:1 H_2O	34.4 (34.0)	2.5 (2.3)	20.1 (19.8)	16.7 (16.6)	24,390
Cu-NO_2[BA]	Brown	$CuC_{10}H_6N_5O_5$	1:1	35.5 (35.3)	1.9 (1.7)	20.2 (20.6)	18.7 (18.7)	25,316
Pd-NO_2[BA]	Yellow	$Pd.C_{30}H_{20}N_{15}O_{16}$	1:3 H_2O	37.9 (37.8)	2.5 (2.1)	22.3 (22.0)	11.2 (11.2)	26,455
-Cl[BA]	Yellow	$C_{10}H_7N_4O_3Cl$		45.1 (45.0)	2.6 (2.6)	21.0 (21.0)		
Co-Cl[BA]	Green	$Co_2C_{10}H_{17}N_4O_9Cl$	2:16 H_2O	24.8 (24.5)	3.5 (3.5)	11.7 (11.4)	23.9 (24.0)	28,902 15,974
Ni-Cl[BA]	Orange	$Ni_2C_{10}H_{11}N_4O_6Cl$	2:1 3 H_2O	27.8 (27.5)	2.7 (2.5)	13.1 (12.8)	26.4 (26.9)	30,303
Cu-Cl[BA]	Brown	$CuC_{10}H_8N_4O_4Cl$	1:1 H_2O	34.8 (34.6)	2.5 (2.3)	16.4 (16.1)	18.3 (18.3)	30,303
-COOH[BA]	Orange	$C_{11}H_8N_4O_5$		48.1 (47.8)	3.4 (2.9)	20.3 (20.3)		
Ni-COOH[BA]	Orange	$Ni_2C_{11}H_6N_4O_5$	2:1	34.0 (33.7)	1.8 (1.5)	14.7 (14.3)	30.7 (29.9)	26,455
Cu-COOH[BA]	Green	$Cu_2C_{11}H_6N_4O_5$	2:1	33.2 (32.9)	1.8 (1.5)	14.2 (13.9)	31.7 (31.7)	28,902
-CHO[BA]	Orange	$C_{11}H_8N_4O_4$		50.9 (50.7)	3.2 (3.1)	21.7 (21.5)		
Co-CHO[BA]	Green	$Co_2C_{11}H_{14}N_4O_8$	2:14 H_2O	29.9 (29.5)	3.6 (3.1)	12.5 (12.5)	26.1 (26.3)	26,455
Ni-CHO[BA]	Orange	$NiC_{11}H_{13}N_4O_7$	1:13 H_2O	35.8 (35.5)	3.9 (3.5)	15.6 (15.1)	15.5 (15.8)	25,000
Cu-CHO[BA]	Brown	$Cu_2C_{11}H_{22}N_4O_{12}$	2:18 H_2O	25.2 (24.9)	4.5 (4.2)	10.8 (10.6)	24.1 (24.0)	23,256
-CH_3[BA]	Yellow	$C_{11}H_{10}N_4O_3$		53.5 (53.6)	4.1 (4.1)	22.4 (22.7)		
Cu-CH_3[BA]	Dark brown	$CuC_{11}H_{11}N_4O_4$	1:1 H_2O	40.7 (40.4)	3.7 (3.4)	17.3 (17.1)	19.6 (19.4)	23,974
Pd-CH_3[BA]	Yellow	$Pd.C_{22}H_{30}N_8O_{12}$	1:26 H_2O	37.8 (37.5)	4.5 (4.2)	16.2 (15.9)	15.0 (15.1)	26,455
Pt-CH_3[BA]	Yellow	$Pt.C_{44}H_{38}N_{16}O_{13}$	1:4 H_2O	44.1 (44.2)	3.0 (3.2)	19.0 (18.8)		26,455
-OH[BA]	Brown	$C_{10}H_8N_4O_4$		48.9 (48.3)	3.0 (3.2)	22.0 (22.5)		

(Continued on next page)

TABLE 1 Analytical Data for Ligands and Its Metal Complexes, Nujol Mull Electronic Spectra (cm^{-1}) and Magnetic Susceptibility *(Continued)*

				% Found (% calculated)				
Compound	Color	Formula	Stoichiometry	C	H	N	M	
Co-OH[BA]	Brown	$Co_2C_{10}H_{18}N_4O_{10}$	2:16 H_2O	25.5 (25.4)	3.7 (3.8)	11.3 (11.8)	24.8 (24.9)	24,390
Ni-OH[BA]	Brown	$NiC_{10}H_9N_4O_5$	1:1 H_2O	37.5 (37.1)	3.0 (2.7)	17.7 (17.3)	18.0 (18.1)	24,390
Cu-OH[BA]	Brown	$Cu_2C_{10}H_{16}N_4O_9$	2:1 5 H_2O	26.3 (25.9)	3.9 (3.4)	12.3 (12.1)	27.6 (27.4)	22,321
-NOH[SBA]	Orange	$C_{11}H_{15}N_5O_6S$		38.0 (38.3)	4.3 (4.3)	20.3 (20.3)		
Pd=NOH[SBA]	Yellow	$Pd.C_{11}H_8N_5O_3S$	1:1	33.5 (33.3)	2.5 (2.0)	17.8 (17.7)	27.6 (26.8)	23,474
-BZd[BA]	Pale yellow	$C_{11}H_{14}N_2O_6$		49.1 (48.9)	5.3 (5.2)	10.2 (10.4)		
Cu-Bzd[BA]	Green	$CuC_{22}H_{14}N_4O_6$	1:2	53.4 (53.5)	3.0 (2.8)	11.6 (11.3)	12.9 (12.9)	28,902
-BZd [SBA]*	Yellow	$C_{11}H_{10}N_2O_5S$		53.1 (52.8)	3.8 (4.0)	11.0 (11.2)		
Co-Bzd[SBA]	Grey	$CoC_{11}H_7N_2O_2S$	1:1	45.8 (45.5)	2.5 (2.4)	09.5 (09.60)	20.5 (20.3)	17,544
Ni-Bzd[SBA]	Pink	$Ni_2C_{11}H_2 1N_2O_9S$	2:1 7 H_2O	28.2 (27.8)	4.5 (4.4)	06.2 (05.9)	24.3 (24.7)	19,455
Cu-Bzd[SBA]	Brown	$Cu.C_{11}H_{15}N_2O_6S$	1:1 4 H_2O	36.2 (36.0)	4.0 (4.1)	07.8 (07.6)	17.3 (17.3)	14,006
-Sal [BA]	Orange	$C_{11}H_8N_2O_4$		57.1 (56.8)	3.1 (3.4)	12.0 (12.1)		
Ni-Sal[BA]	Green	$Ni_2C_{11}H_{13}N_2O_7$	2:1 $3H_3O$	33.0 (32.8)	3.5 (3.2)	06.2 (06.9)	29.3 (29.2)	24,390
Cu-Sal[BA]	Pale green	$Cu_2.C_{11}H_{12}N_2O_7$	2:1 $3H_2O$	32.3 (32.1)	3.1 (2.9)	07.0 (06.8)	30.8 (30.9)	28,902
-Sal [SBA]**	Pale yellow	$C_{11}H_8N_2O_5S$		53.4 (53.2)	3.7 (3.2)	11.6 (11.3)		
Co-Sal[SBA]	Brownish green	$CoC_{11}H_9N_2O_4S$	1:1 H_2O	40.2 (40.7)	2.5 (2.7)	08.5 (08.6)	18.2 (18.2)	17,065
Ni-Sal[SBA]	Olive green	$NiC_{11}H_7N_2O_3S$	1:1	43.5 (43.2)	2.5 (2.3)	09.5 (09.2)	19.2 (19.2)	18,051
Cu-Sal[SBA]	Grey	$CuC_{11}H_7N_2O_3S$	1:1	42.2 (42.5)	2.8 (2.3)	09.2 (09.0)	20.2 (20.4)	28,902
Pd-Sal[SBA]	Brown	$Pd.C_{11}H_8N_5O_3S$	1:1 6 H_2O	28.8 (28.6)	4.7 (4.1)	06.1 (06.1)	23.4 (23.1)	26,455
Pt-Sal[SBA]	Buff	$Pt.C_{44}H_2 8N_8O_{12}S_4$	1:4	44.0 (44.6)	2.5 (2.4)	09.5 (09.5)		26,455

[a] The % of sulphur content found/calculated = 12.3 (12.8).

Preparation of Metal Complexes

An ammoniacal solution of the metal (II) chloride (Co, Ni, Cu, Pd and Pt) (0.1 mol) was mixed with the organic compounds (1, 2) (0.1 mol), which are dissolved in dioxane. The reaction mixture was boiled under reflux for 1 hr., then left overnight, whereupon the complex is precipitated. The complexes (Table 1) were separated by filtration, washed several times with water, and dried in vacuum over P_4O_{10}.

Analysis and Instruments

The analytical data are collected in Table 1. All the complexes do not contain anions with the melting point above 300°C. Metal contents were determined as described previously.[18] The $Pd^{[II]}$ content was determined gravimetrically as the dimethylglyoximato complex.[18] C, H, and N analyses were made by the chemistry department, Faculty of Science, Cairo University. Electronic spectral measurements of the solid complexes were recorded using a Pye Unicam Spectrophotometer Model SP 1750 and Cary Model 14. The solvents used for studying the Racah parameters are of spectroquality grade. IR spectra were taken as KBr disc using SP 2000 Pye Unicam instrument covering the 200–4000 cm^{-1} range. ESR spectra of the copper complexes were measured at 298 K using a Varian E-12 instrument (X-band) spectrometer (2,2-diphenyl-1-picryl hydrazone) was used as an external standard. Molar magnetic susceptibilities, corrected for diamagnetism using Pascal's constants, were determined at room temperature (298 K) using Gouy's method. The apparatus was calibrated with Hg [Co $(SCN)_4$].

Stereochemistry of the Complexes

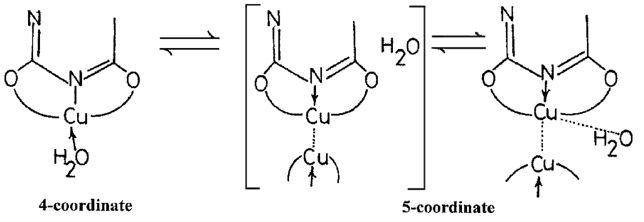
Cobalt Complexes. The analytical data shown in Table 1 indicated three different stoichiometries (metal: ligand nH_2O). However, most of the complexes are with large number of water molecules. From the spectral and magnetic moment values, the complexes are classified to three categories (Table 1):

1. Pure T_d obtained from -CHO (BA), -Bzd(SBA), -Sal(SBA), and -Bzd(SBA) compounds. All of them are with the electronic transition of the type $^4A_{2g} \rightarrow {}^4T(P)$.[13]
2. Pure O_h depicted from $-NO_2$ (BA) and -Cl(BA) compounds, with the transitions $\nu_3 = {}^4T_{1g} \rightarrow {}^4T_{1g}$ (P) and $\nu_2 = {}^4T_{1g} \rightarrow {}^4A_{2g}$.[5–7]
3. An equilibrium between T_d and O_h geometries obtained from -OH (BA) complex, with the electronic transitions $^4A_2 \rightarrow {}^4T_1$ (P), $^4T_{1g}$ (F) $\rightarrow {}^4A_{2g}$ (F), and $^4T_{1g}$ (F) $\rightarrow {}^4T_{1g}$(P).[6,7]

Nickel Complexes. The analytical data shown in Table 1 indicate three different stoichiometries (metal: ligand nH_2O), depending on the substituents. The great similarities between the electronic absorption spectra of these complexes, either in position or in intensity, suggest similar stereochemistry, except-Bzd(SBA) and -Sal(BA).[19] The electronic spectra gathered with the μ_{eff} values of the azo complexes containing -NO_2 (BA), -Cl(BA), -COOH(BA), -CHO(BA), -CH_3(BA), -OH(BA), and -Sal(SBA) groups, suggest the presence of different geometries, viz. tetrahedral and square planar.[7,8] Some of the complexes are with +1 and/or +2 oxidation states of nickel.

The diamagnetic property and the electronic spectra of -Bzd(SBA) and -Sal(BA) complexes suggest their existence in square planar geometry, and the ligands are of strong field property to quench the distribution of charge density,[19] with the possible existence of Ni^1 in -Bzd(SBA). The unusual data for this complex permit the assumption for association where spin quenching occurs. The 2:1 nH_2O nickel orange complexes are obtained from the -Cl(BA) and -COOH(BA) azo ligands. The first gives two bands at 30,303 and 23,529 cm^{-1} in a broad feature, while the second gives only one intense band at 264,550 cm^{-1}. The broad nature of the longer wavelength band of the chloro complex is argued to the presence of more than d-d transition.[19] However, the absence of this band in the carboxy complex is probably due to its existence in an associated structure through intramolecular hydrogen bond.

Copper Complexes. The copper complexes (Table 1) derived from -NO_2(BA), -CHO(BA), -OH(BA), and -Sal(SBA) have a tetrahedral geometry. However, -Cl(BA), -Me(BA), -Sal(BA), -(COOH), and -Bzd(BA) exist in a dynamic equilibrium between the fourth and fifth coordinate (structure 3) and that -Bzd(SBA) is with tetragonal distorted octahedral stereochemistry.[20]



Additional information is derived from electron spin resonance data. The temperature has no effect on the spectrum of all complexes except that of the copper -Sal(SBA). The increase in temperature leads to decrease the G and $\langle g \rangle$ values by 0.1 and 0.01, respectively. However, $g_{\perp}$ remains the same and g'' is decreased by 0.03 unit on increasing the temperature, which agreed with an orbitally non-degenerate ground state. $\langle g \rangle$ values lie in the range

TABLE 2 Electronic Spectral Resonance Data for Copper Complexes (298 K)

Copper complexes	g_{11}	$g_{\perp}$	$\langle g \rangle$	G	g_s
Cu-Cl(BA)	2.207	2.185	2.190	1.120	
Cu-NO_2(BA)	2.189	2.176	2.180	1.070	
Cu-COOH(BA)	2.190	2.175	2.180	1.080	
Cu-CHO(BA)	2.194	2.175	2.180	1.108	
Cu-OH(BA)	2.210	2.176	2.190	1.190	
Cu-CH_3(BA)	2.190	2.070	2.110	2.710	
Cu-Bzd(BA)	—	—	—	—	2.175
Cu-Bzd(SBA)	—	—	—	—	2.180
Cu-Sal(SBA)	2.270	2.180	2.210	1.500	
	2.300	2.180	2.220	1.600[a]	

[a] The experiment was done at −170 K.

2.11–2.22. All the complexes exhibit an axial elongated type spectrum with $d_x2\text{-}_y2$ ground state ($g_{\perp}$ and $g_{//}$) except those of -Bzd(BA) and -Bzd(SBA), where only one g value is obtained (2.175 and 2.180, respectively). The latter two cases of copper (II) complexes may exist in dynamic or pseudo rotational types of Jahn–Teller distortion.[21]

The ESR spectra of -Sal(SBA) and -CH_3(BA) complexes are of a broad nature and with strong covalency in bonding. All the complexes have much lower G values ($G \ll 4$) due to strong interaction between copper and the active centers of the organic compounds. However, no hyperfine structure is seen and no absorption is observed at 1600 Gauss to assign the $M_s = \pm 2$ transitions in the copper (II) dimer. In general, the spectra showed a very intense sharp absorption band at ≈3100 G that arises from the copper (II) ions in a spin state $S = 1/2$. The -Bzd(BA) and -Bzd(SBA) copper complexes give no change in the ESR pattern (Table 2).

Palladium Complex. The great similarity of the electronic spectral band and the diamagnetic property of these complexes (Table 1) lead to a similar stereochemistry with square planar geometry.[22,23] The 1:4. $4H_2O$ Pd-(SBA) complex gives two electronic absorption bands at 29,940 and 24,631 cm^{-1}. The slight change in the position of the spectral bands from -(BA) and -(SBA) palladium complexes is due to the change in the electronegativity of O and S atoms[8] (Table 1). The 1:1 Pd-H[BA] gives two intense bands at 26,455 and 17,544 cm^{-1}. The longer wavelength is due to strong conjugation in the complex with the presence of the azo chromophore. These bands are of spin allowed d-d transition. The tridentate nature of the organic compound with possible Pd-Pd interaction gathered with its diamagnetic property are consistent with square planar geometry in 1:1H-(BA), = NOH(SBA), and -Sal(SBA) palladium complex. In 1:3 and 1:4 Pd complexes, the square planar geometry of (BA), (SBA), -NO_2 (BA) azo palladium complexes lead to bidentate behavior of the first two ligands on complexation. These complexes are hydrogen-bonded with the other ligand and water molecules.

Platinum Complexes. The prepared platinum complexes (Table 1) are of [1:1. nH_2O) derived from -(BA), -(SBA), and -H(BA), and (1:4 . nH_2O) derived from -CH_3 (BA), and -Sal (SBA). The ground state of $PtCl_4{}^{2-}$ with D_4h symmetry is $^1A_{1g}$. Three stronger spin-allowed and the three spin-forbidden d-d transitions are as follows:

$$^3A_{2g}\text{: } {}^1A_{1g} \rightarrow {}^1A_{2g}(\nu_1 = 21,000\ \text{cm}^{-1}, \varepsilon = 15)$$

$$^3B_{2g}\text{: } {}^1A_{1g} \rightarrow {}^1B_{2g}(\nu_2 = 25,000\ \text{cm}^{-1}, \varepsilon = 59)$$

$$^3E_{2g}\text{: } {}^1A_{1g} \rightarrow {}^1E_{g}(\nu_3 = 30,2000\ \text{cm}^{-1}, \varepsilon = 64)$$

The first band is reasonably assigned to the spin-forbidden transition because of its low intensity. The third and fourth bands are due to spin-allowed transitions, $d_z2 \rightarrow d_x2\text{-}_y2$ ($^1A_{2g}$) and d_{xz}, $d_{yz} \rightarrow d_x2\text{-}_y2$ (^1E_g), respectively.[7] The second band can be assigned to a spin-forbidden, $^3E_{2g}$ or $^3A_{2g}$, and the other to a spin-allowed [$d_z2 \rightarrow d_x2\text{-}_y2$ ($^1B_{2g}$)] transition. Although the intensity of a spinforbidden band is much weaker than that of a spin-allowed, the platinum complexes give fairly strong spin-forbidden bands owing to a strong spin-orbit interaction. However, band 2 is assigned to a spin-forbidden transition.[24] The prepared platinum complexes (Table 1) are of (1:2. nH_2O) derived from -(BA), -(SBA), and -H(BA), and (1:4. nH_2O) derived from -CH_3(BA) and -Sal(SBA). The ground state of $PtCl_4{}^{2-}$ with D_4h symmetry is A_{1g}. The band $^3A_{2g}$ due to transition of $A_{1g} \rightarrow {}^1A_{2g}$ (ν_1 = 21,000 cm^{-1}) ($\varepsilon = 15$) is of a spin-forbidden transition. The intensity of spin-forbidden is much weaker than that of a spin-allowed, so the platinum complexes give fairly strong spin-forbidden bands owing to a strong spin orbit interaction.[7] The 1:2 Pt-(SBA) and Pt-(BA) complexes absorb at 29,240 and 19,920 and 29,240 cm^{-1}, respectively, where the former complex exists in a more stabilized and conjugated structure than the latter due to the difference in electronegativity between oxygen and sulphur atoms. The 1:2 Pt-H(BA) complex absorbs at 24,390 cm^{-1}.

The absence of anions in the synthesized complexes, suggest that Pt^{IV} is subjected to reduction, where Pt^{II} is formed. The electronic spectra of the platinum complexes (Table 1) suggest square planar geometry with D_4h symmetry.

The infrared spectra of the metal complexes with those of the free ligands, the vibrational frequency of coordinated functional group (e.g., ν_{O-H}, $\nu_{C=O}$, $\nu_{C=N}$, $\nu_{C=S}$, ν_{COO^-} and $\nu_{N=N}$), are affected with different degrees depending on the strength of π interaction occurring between the metal ion and π electron of functional group.[19] Some of the carbonyl bands disappeared and others are slightly shifted, probably due to tautomerization to the enol form followed by complexation through the deprotonaion process. The shift in C=N bands suggested the C=N is involved in coordination.

Most of the $\nu_{N=N}$ bands are not affected by complexation, except in (Cu, Co-CHO), (Ni, Cu-COOH), and (CO, Ni-Cl). The ν_{NH}, ν_{OH}, ν_{OH}, ν_{N-H}, and ν_{C-O} are affected on coordination which suggests that the oxygen and nitrogen and/or S atoms are considered as centers for complexation. In few cases, the ligand may act as bidentate, as in structure (4). The tridentate behavior exists in most complexes where the azo group is not involved in the chelation, structure (5). The ligands act as mixed bidentate-tridentate, where the azo group is either involved, structure (6), or is not involved structure (7)) and structure (8). Moreover, the ligand acts as a tri-tridentate, structure (9).

The electronic absorption spectra of cobalt complexes are recorded in presence of different solvents to trace the possible adducts formed,[25] beside the calculation of Racah parameters, to know the geometry of new species and their strengths.[26] The calculations of the ligand field parameters are as follows:

$$10\ D_q = \nu_2 - \nu_1, \quad B = \left(2\nu_1^2 - \nu_1\nu_2\right)/(12\nu_2 - 27\nu_1)$$

$$10\ D_q = 2\nu_1 - \nu_3 + 15B, \quad B = 1/30[-(2\nu_1 - \nu_3) \pm \left(-\nu_1^2 + \nu_3^2 + \nu_1\nu_3\right)^{1/2}]$$

$$10\ D_q = 1/3(2\nu_2 - \nu_3) + 5B, \quad B = 1/510\left\{7(\nu_3 - 2\nu_2) \pm 3\left[81\nu_3^2 - 16\nu_2(\nu_2 - \nu_3)\right]\right\}$$

$$10\ D_q = \nu_2 - \nu_1, \quad B = (\nu_2 + \nu_3 - 3\nu_1)/15$$

The data are collected in Table 3, where the followings are given: Most of the B parameter, which is the measure of the electron-electron repulsion term which is lower in complexes (Table 3), than in the free ion (985 cm^{-1}), with β values lower than unity, assume largely covalent bonds between the organic ligand and the metal ion.[25] The -NO_2 complex with ν_2/ν_1 values in the presence of all basic solvents lie between 1.86 and 2.08 suggests that complex-solvent interaction still has an O_h structure. However, the ν_2/ν_1 value 1,2-dichloro ethane is 1.45 to identify the tetrahedral geometry. The chloro complex remains of O_h geometry, irrespective of the basic solvents used.

The methods used to calculate the Racah parameters in presence of different solvents for nickel complexes are as follows:

$$10D_q = \nu_1, \quad B = \left(2\nu_1^2 + 2\nu_2^2 - 3\nu_1\nu_2\right)/(15\nu_2 - 27\nu_1)$$

$$10D_q = \nu_1, \quad B = \left(2\nu_1^2 = \nu_3^2 - 3\nu_1\nu_3\right)/(15\nu_3 - 27\nu_1)$$

$$10D_q = \nu_1, \quad B = (\nu_2 + \nu_3 - 3\nu_1)/15$$

$$10D_q = \nu_1, \quad B = 1/75\left[3\nu_1 \pm 25(\nu_3 - \nu_2)^2 - 16\nu_1^2\right]^{1/2}$$

TABLE 3 Racah Parameters for the Solvent Effects on the Electronic Spectra of Cobalt Complexes

Complex/media	Method of calculation	ν_1	ν_2	ν_3	B	β	10 D_q	ν_2/ν_1
Co-No_2(BA)								
1,2-Dichloroethane	(c)	5625	8188	16,267	880	0.89	4436	1.45
pyridine	(b)	9410	17,500	19,375, 21,875	828	0.84	10615	1.86
	(c)				904	0.92	9312	
	(d)				660	0.67	8090	
α Picoline	(b)	8750	16,500	19,375	779	0.79	9810	1.88
	(c)				851	0.86	8797	
	(d)				642	0.65	7750	
β Picoline	(b)	8750	16,600	19,000	757	0.77	9855	1.89
	(c)				818	0.83	8823	
	(d)				623	0.63	7850	
γ Picoline	(b)	8140	16,900	20,300	618	0.63	5250	2.08
	(c)				901	0.92	9005	
	(d)				852	0.86	8760	
Propylamine	(d)	8140	16,250	21,250	872	0.89	8110	1.99
Butylamine	(b)	8820	16,800	20,118	831	0.84	9987	1.90
	(c)				882	0.89	8904	
	(d)				697	0.71	7980	
Co-CHO(BA)								
Methylamine	(b)	10,000	15,500	19,500	710	0.72	11,150	1.55
Acetonitrile	(b)	9500	15,750	19,250	726	0.74	10,640	1.66
DMF	(b)	9750	14,500	18,500	656	0.67	10,840	1.49
Pyridine	(b)	9250	15,500	19,250	742	0.75	10,380	1.68

Co-Cl (BA)								
Pyridine	(c)		15,000,11,400	19,300	959	0.97	7162	1.46
α Picoline	(c)	11,000	14,900	20,600	980	0.99	7967	1.35
β Picoline	(b)	9300	11,600	22,200,14,700	945	0.96	10,575	1.41
	(d)				497	0.50	3850	
γ Picoline	(b)	11,500	12,800, 15,700	20,600	687	0.69	12,705	1.24
Co-OH(BA)								
1,2-Dichloroethane	(c)	6000	8000, 10,800	14,800,15,400, 16,800, 19,000	862	0.87	5077	1.57
	(d)				527	0.53	3400	
Pyridine	(c)	9000	16,200	19,600	875	0.89	8642	1.80
	(d)				587	0.59	7200	
α Picoline	(c)	9000	16,000	19,200	854, 547	0.87, 0.55	8535, 7000	1.78
β Picoline	(c)	9000	16,200	19,500	869	0.88	8645	1.80
	(d)				580	0.59	7200	
γ Picoline	(c)	8200	14,100, 16,100	20,200	957	0.97	8052	
	(d)				707	0.72	6800	
Propylamine	(c)	8200	15,500	20,300	944, 747	0.96, 0.76	8287, 7300	1.89
Bytylamine	(d)	8200	15,600,16,600	20,700, 21,700	847	0.86	7900	1.96

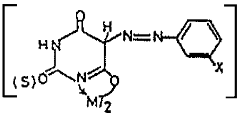
TABLE 4 Racah Parameters for the Solvent Effects on the Electronic Spectra of Nickel Complexes

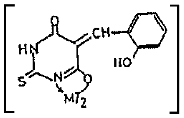
Complex/media	Method of calculation	ν_1	ν_2	ν_3	B	β	ν_2/ν_1
Ni-COOH (BA)							
Butylamine	(a)	13,200	18,750	24,750	565	0.55	1.42
γ Picoline	(a)	12,857	19,250	23,917	704	0.68	1.49
DMF	(a)	12,500	19,250	24,500	796	0.77	1.54
Pyridine	(c)	11,900	20,400	24,750	630	0.61	1.71
Ni-No$_2$(BA)							
DMSO	(b)	7,250	13,750	24,000	968	0.93	1.89
DMF	(c)	1000	17,750	25,000	850	0.81	1.78
Pyridine	(c)	9000	14,750	23,500	750	0.72	1.64
α Picoline	(c)	9500	15,125	23,250	658	0.63	1.59
β Picoline	(c)	9000	15,125	23,500	775	0.74	1.68
γ Picoline	(c)	9500	15,125	25,500	808	0.77	1.59
Ni-CHO(BA)							
DMSO	(a)	12,000	16,500	24,500	441	0.43	1.38
	(c)				333	0.32	
DMF	(a)	10,700	15,000	22,500	431	0.42	1.40
	(c)				360	0.35	
Pyridine	(c)	9375	14,500	25,500	792	0.77	1.55
1,2-Dichloroethane	(d)	8000	16,125	26,666	878	0.84	2.01
Ni-Cl(BA)							
Butylamine	(c)	9500	16,550	24,500	837	0.81	1.74
γ Picoline	(c)	9625	16,837	24,250	814	0.79	1.75
Pyridine	(c)	9400	15,100	25,250	743	0.72	1.61
Ni-OH(BA)							
α Picoline	(c)	9250	15,875	22,875	733	0.70	1.73
β Picoline	(c)	9750	16,750	23,417	728	0.69	1.72
γ Picoline	(c)	9625	15,125	23,375	642	0.61	1.57
DMSO	(b)	7750	16,417	24,500	953	0.91	2.12
DMF	(c)	7750	15,000	22,600	957	0.92	1.93
Pyridine	(c)	8000	13,750	22,125	792	0.76	1.72
Ni-Sal(BA)							
Butylamine	(a)	12,500	18,500	25,500	650	0.63	1.48
Propylalmine	(a)	12,000	18,750	24,750	829	0.80	1.56
α Picoline	(a)	12,500	18,000	24,500	570	0.55	1.44
Pyridine	(a)	10,000	15,500	24,250	660	0.64	1.55
Ni-Bzd(SBA)							
Butylamine	(c)	7500	11,500	18,000	467	0.45	1.53
DMSO	(c)	7000	12,000	18,500	633	0.61	1.71
DMF	(b)	7250	13,000	17,375	575	0.55	1.79
Pyridine	(a)	7500	13,250	26,830	683	0.56	1.76

The β values are less than unity (Table 4), suggesting a largely covalent bond between the organic ligand and nickel.[27] The electronic absorption spectra of nickel complexes were consistent with the formation in tetragonal distorted octahedral geometry in case of -NO$_2$, -COOH, -CHO, and -OH (in case of γ-picoline only), octahedral geometry in -OH substituted ligand in most solvents, Ni-Sal (BA) complex in pyridine, α-picoline,

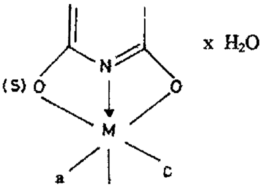
A-Bidentate ligand

B-Tridentate ligand





(4)



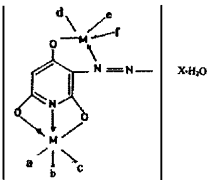
(5)

-(BA)	M	Pd, X = 2 moles (BA)	-	M = Co	a = b = c = H_2O	
	=	Pt, X= zero	NO_2(BA)	M= Ni	a= H_2O	x= $5H_2O$
				M= Cu	a= —	b= c= x= zero
-(SBA)	M	Pd, X= 2 moles (SBA)	-CI(BA)	M= Cu	a= H_2O	b= —
	=	+4 H2O	-	M= Ni	a= H_2O	c= x= zero
		Pt, X= zero	CHO(BA)	M= Cu	a= H_2O	b= c= zero
						= $2H_2O$
			-			b= —
			CH_3(BA)			c= x= zero
-H(BA)	M	Pt, X= 7 H_2O	-	M= Ni	a= H_2O	b= c= x= H_2O
	=		OH(BA)	M= Cu	a= mono-	b= c= x= zero
			-	/2	bidentate	
					legand	
			Bzd(BA)			
	M	Pd, X= 6 H_2O	-	M= Co	a= —	b= c= x= zero
CH_3(BA)	=	Pt, X= 2 moles-	Bzd(SBA)	M= Cu	a= b= c	
					= x= H_2O	
		CH_3(BA) + H_2O	-	M= Co	a= H_2O	b= c= x= zero
			Sal(SBA)			
-	M	Pd, X= -NO_2(BA) +H_2O		M= Ni	a= —	b= c= x= zero
NO_2(BA)	=			M= Cu	a= —	b= c= x= zero
-(SBA)	M	Pt, X= 2 moles -	-H(BA)	M= Pd	a= Pd	b= c= x= zero
	=	Sal(SBA)	= NOH(SBA)	M= Pd	a= Pd	b= c= x= zero
				M= Pd	a= H_2O	b= c= x= H_2O
			Sal(SBA)			

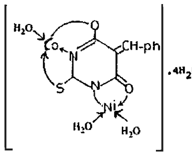
C-Mixed bidentate-tridentate ligand

i) Azo group is involved

iii) -Bzd (SBA)



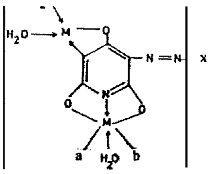
(6)



(8)

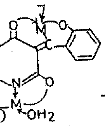
-Cl(BA)	M=Co	a=b=c=e=f=H_2O	....
	M=Ni	a=d=e=H_2O	b=c=f=x=zero
-CHO(BA)	M=Co	a=d=e=H_2O	x=H_2O
	M=Cu	a=d=e=H_2O	x= $5H_2O$
-COOH(BA)	M=Ni	a=d=e=----	b,c,f,x=zero
	M=Cu	a=d=e=----	b,c,f=zero

-........... **Association**



(7)

-OH(BA) M=Co a=b=x=H_2O
M=Cu a=b=x=zero x=$2H_2O$



(9)

-Sal(BA) M=Ni and Cu

propylamine, and butylamine solvents. The Ni-Bzd(S) complex forms adducts with butylamine, DMSO, DMF, and pyridine solvents with the tracing of square pyramidal geometry. However, the (ν_2/ν_1) values in presence of DMSO, DMF, and pyridine solvents are in the range of 1.71–1.79, which suggests the possible existence of O_h geometry. So the following equilibrium is established: square pyramidal $\leftrightarrow$ octahedral.[22,26,27] The e_g electrons will become σ-antibonding, and spend some time on the organic compound. The t_{2g} electrons may become π-bonding or antibonding and spend some time on the organic moiety. So, a small amount of the σ and π electron density on the metal may be transferred into the ligand. Such delocalization will increase the mean distance between the d electrons to reduce the value of β.[23] For -NO_2 (BA) complex, the most distorted complex is that in presence of α and γ picolines solvents, while the least distorted is that studied in DMSO. Similarly, the nickel Cl-(BA) complex gives adducts with butylamine, γ picoline, and pyridine solvents, which are of a tetragonal distorted octahedral geometry. The butylamine-nickel adduct gives more split bands, and nickel pyridine adduct is the most distorted, probably due to possible existence of some sort of isomerization. This is subject to change the bond length, and the bond angle gathered with the variation in the population in the electron density in such a system.[27] A similar situation is reached for the -COOH(BA) and -CHO(BA) complexes. The nickel -OH(BA) complex gives octahedral adducts with pyridine, DMF, DMSO, and α and β picolines. However, the γ picoline adduct has a tetragonal distorted geometry. The nickel Sal(BA) complex with pyridine, α picoline, propylamine, and butylamine formed octahedral adducts. The ν_3 and ν_2 bands in the presence of propylamine and butylamine bases are of a split nature. The ν_1 band in the presence of propylamine is splitted, while that in the presence of butylamine is of a broad nature, so such trend is related to the chain length of the amine.

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