

Mixed Ligand Complexes of Pt(II) with Biguanide & Triphenylphosphine

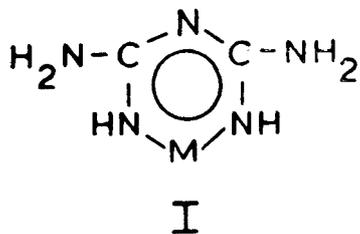
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A series of tetravalent cationic mixed ligand complexes of platinum(II) with triphenylphosphine and biguanide has been synthesized and characterized. The formation of stable colourless complexes of metal with biguanide and triphenylphosphine is attributed to the strong metal-nitrogen and metal-phosphorous bonds with $p\pi-d\pi$ donation from ligand biguanide supplemented by $d\pi-d\pi$ back donation from metal to triphenylphosphine. The relative positions of energy levels of biguanide and triphenylphosphine with respect to metal d -orbital and the influence of metal d -orbital on the π -bonding ligands have been taken into consideration to interpret the IR and UV spectral shifts. The behaviour of coordination of platinum(II) complexes with π -electron excess and π -electron deficient ligands suggests the π -electron delocalization over the whole complex molecule through ligand-metal-ligand interaction explaining the phenomena of electromeric effect of triphenylphosphine over the metal-biguanide aromatic ring.

THE complex forming capacity of biguanide and substituted biguanides with bi- and ter-valent metals has already been reviewed¹. The possibility of π -electron delocalization in metal biguanides has been suggested by Sen² from a consideration of the extension of π -conjugation of the biguanide molecule through the metal d -orbitals as shown in structure (I).



The ligational characteristics of biguanide is, hence, governed not only by the π -donor capacity of nitrogen but also by the participation of dative π -bond of biguanide and monoprotonated biguanide in metal ligand bond formation. It was considered interesting to study the involvement of this π -bond under the influence of electron attracting groups attached to the central metal atom. Attachment of such a ligand to the central metal atom will influence the ring current in metal biguanides. The present study is aimed at finding out qualitatively the effect of such changes in the delocalized π -system of metal-biguanides under the influence of other ligands.

The coordinating capacity of tertiary phosphine with platinum was reported by Cahour and Gal³ as early as 1870. Tertiary phosphines have played

an important role in coordination chemistry for its complex forming ability by its synergic effect through the participation of vacant d -orbital of phosphorus with the filled metal d -orbital.

Although D_4 symmetry has been maintained in most of the complexes of Pt(II) with a variety of ligands, Morgan and Burstall⁵ have claimed the quasi-octahedral symmetry in $\text{Pt}(\text{bipy})_2\text{I}_2$. Biguanide was shown² to coordinate with platinum metals in +2 oxidation state. Platinum(II) has also been reported to form a variety of complex compounds with triphenylphosphine⁴.

Mixed ligand complexes of Pt(II) with phosphine and halogen such as $\text{Pt}(\text{PR}_3)_2\text{X}_2$ (where R = alkyl or aryl group, X = halogen); phosphine-sulphur such as $[\text{Pt}(\text{PR}_3)_2(\text{thiourea})_2]\text{X}_2$ and phosphine-amine such as $[\text{Pt}(\text{PEt}_3)_2(\text{NH}_3)_2]\text{Cl}_2$, $\text{PtX}_2(\text{PR}_3)_2$ are known⁴. With nitrogen containing chelating ligands, the only known example⁶ is $[\text{Pt}(\text{PPh}_3)_2\text{en}]^{+2}$ (where en = ethylenediamine). The compound being unstable, the detailed study in solution is lacking. Mixed ligand complexes of platinum(II) with triphenylphosphine and nitrogen donor chelating ligands having π -interaction are unknown. Moreover, the effect of π -donating ligand on the stabilization of Pt(II) with d^8 configuration in the presence of π -accepting ligand has not yet been studied. It was hence, thought interesting to study the mixed ligand complexes of Pt(II) with biguanide and triphenylphosphine.

Materials and Methods

The compound, *cis*- $\text{PtCl}_2(\text{PPh}_3)_2$, was prepared following the literature method⁷. Biguanide and substituted biguanide normal sulphates were prepared according to the methods described by Ray¹. The reagents used were of analytical grade. The conductances were measured by Philips conducto-

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metric bridge. The magnetic measurements were made with a Guoy balance at room temperature. The electronic spectra were recorded with UV-spec Hilger and DU-2 spectrophotometer and the IR spectra were taken in the region 3500-600 cm⁻¹ with a Perkin-Elmer 421 spectrophotometer.

cis-Bis(triphenylphosphine)(biguanidinium)platinum(II) hydroxide — Biguanidine normal sulphate (3 g) was dissolved in 1:1 ammoniacal water (200 ml). *cis*-Pt(PPh₃)₂Cl₂ (7 g) was suspended into this cold ammoniacal biguanide solution and the suspension warmed with stirring on a water-bath, whereby a major part of the solid dissolved. It was filtered while hot, washed with warm water and the washings alongwith the filtrate cooled to room temperature and finally kept overnight in a refrigerator. Voluminous fine needle shaped colourless crystals separated from the solution. They were filtered and washed with cold water and dried over sodium hydroxide pellets in a desiccator. The yield was 6.4 g (80%) on the basis of *cis*-Pt(PPh₃)₂Cl₂. Tris- and tetrakis-(triphenylphosphine)platinum were the major side products. The compound is sparingly soluble in cold water, but highly soluble in hot water, methanol, nitrobenzene, nitromethane and other polar solvents.

cis-Bis(triphenylphosphine)(biguanidinium)platinum(II) sulphate — The base, *cis*-[Pt(BigH)(PPh₃)₂](OH)₂ was dissolved in boiled water. Ammonium sulphate was added to it. The solution was filtered and concentrated on a water-bath. On cooling the concentrated solution to room temperature, colourless needle shaped crystals separated out. The crystals were washed, dried and analysed.

cis-Bis(triphenylphosphine)(biguanidinium)platinum(II) chloride — The chloride was prepared in the same way as the sulphate using ammonium chloride in place of ammonium sulphate.

cis-Bis(triphenylphosphine)(biguanidinium)platinum(II) iodide — To an aqueous suspension of *cis*-Pt(PPh₃)₂Cl₂ (2 g), potassium iodide solution was added and the suspension warmed over a steam-bath till the whole mass was converted into yellow insoluble solid. The yellow mass was washed several times with distilled water for complete removal of chloride, iodide and potassium ions. It was then dried and analysed.

This compound may also be prepared by (i) heating the base, *cis*-[Pt(BigH)(PPh₃)₂](OH)₂ with ammonium iodide in aqueous medium on a water-bath and (ii) neutralization of the base, *cis*-[Pt(BigH)(PPh₃)₂](OH)₂ with hydroiodic acid and warming the mixture on a water-bath.

The compound is sparingly soluble in water, highly in nitrobenzene and nitromethane, but insoluble in alcohols.

cis-Bis(triphenylphosphine)(biguanidinium)platinum(II) bromide and cis-bis(triphenylphosphine)(biguanidinium)platinum(II) nitrate — These were prepared following the same method as that for chloride using the appropriate ammonium salts.

cis-Bis(triphenylphosphine)(biguanidinium)platinum(II) bisulphate — The compound was prepared by adding excess sulphuric acid to the base *cis*-[Pt-(BigH)(PPh₃)₂](OH)₂ and warming on a water-bath.

cis-Bis(triphenylphosphine)(diethylbiguanidinium)-platinum(II) hydroxide — Diethylbiguanide normal sulphate (4.5 g) was dissolved in 20 ml of 2% sodium hydroxide solution. *cis*-[PtCl₂(PPh₃)₂] (7 g) was suspended into this alkaline solution. On slight warming, a major part of the solid dissolved. The filtered hot solution was slowly cooled to room temperature and kept overnight in the refrigerator. Colourless fine needle shaped crystals separated from the solution. These were filtered, washed with cold distilled water and finally dried over sodium hydroxide in a desiccator.

cis-Bis(triphenylphosphine)(diethylbiguanidinium)-platinum(II) sulphate, cis-bis(triphenylphosphine)(diethylbiguanidinium)platinum(II) chloride and cis-bis(triphenylphosphine)(diethylbiguanidinium)platinum(II) bisulphate — These were prepared in the same way as the corresponding biguanide complexes using in each case the original compound, *cis*-bis-(triphenylphosphine)(diethylbiguanidinium)platinum(II) hydroxide, in place of *cis*-bis-(triphenylphosphine)(biguanidinium)platinum(II) hydroxide.

cis-Bis(triphenylphosphine)(phenylbiguanidinium)-platinum(II) hydroxide — Phenylbiguanide normal sulphate (5 g) suspended in water (200 ml) was treated with 2% solution of sodium hydroxide when a clear alkaline solution was obtained. *cis*-PtCl₂(PPh₃)₂ (7 g) was suspended into the cold alkaline biguanide solution. On slight warming a part of the solid was dissolved and the mass filtered while hot. The residue was washed several times with hot water. The washings were collected along with the original filtrate and cooled slowly to room temperature and finally kept overnight in a refrigerator. Colourless fine needle shaped crystals were separated and collected in a gooch crucible after washing with distilled water. The crystals were dried over potassium hydroxide pellets in a desiccator.

The base decomposes readily in hot aqueous solutions. The salts of the above complex could not be isolated because of its instability.

The elemental analytical data of all the biguanide complexes have been summarized in Table 1.

Results and Discussion

The high stability of the complex cation *cis*-[Pt(BigH)(PPh₃)₂]²⁺ in cold and hot water as well as in acid solution (pH 3.5) indicates that the stability of the biguanide ring is due to its strong π-interaction (*cis*-effect) with the metal *d*-orbital as against the *trans* effect of two triphenylphosphine groups at the opposite side of the biguanide ring.

The conductivity measurements of the complexes in aqueous and nonaqueous medium indicates that hydroxo-, chloro- and bromo-complexes are bi- and univalent electrolytes, whereas the sulphates are bi-bivalent electrolytes.

That the triphenylphosphine and not its oxide is coordinated to the platinum atom in this series of complexes is realized from the fact that (i) in the IR spectra the characteristic band at 1125 cm⁻¹ due to 4-coordinated phosphorus in triphenylphosphine oxide and its complexes⁸ is absent; (ii) sharp bands are obtained in the region 1190 to 1000 cm⁻¹ and there is no extra band for νP-O

TABLE 1 — ANALYTICAL DATA OF THE VARIOUS COMPLEXES

Compounds	Found (%)				Reqd (%)			
	Pt	N	P	Anion	Pt	N	P	Anion
[Pt(BigH)(PPh ₃) ₂](OH) ₂	22.98	8.15	7.12	—	22.82	8.19	7.22	—
[Pt(BigH)(PPh ₃) ₂]Cl ₂	22.36	7.65	6.87	7.45	21.91	7.85	6.96	7.46
[Pt(BigH)(PPh ₃) ₂]SO ₄	22.02	7.24	7.03	9.98	21.31	7.64	6.77	10.48
[Pt(BigH)(PPh ₃) ₂](NO ₃) ₂	21.23	9.93	7.22	—	20.65	10.37	6.56	—
[Pt(BigH)(PPh ₃) ₂](HSO ₄) ₂	19.51	6.61	6.18	19.03	19.25	6.90	6.11	18.92
[Pt(MeBigH)(PPh ₃) ₂](OH) ₂	23.45	8.05	7.43	—	22.90	8.22	7.28	—
[Pt(MeBigH)(PPh ₃) ₂]Cl ₂	22.01	8.15	6.71	7.81	21.57	7.73	6.85	7.84
[Pt(MeBigH)(PPh ₃) ₂]SO ₄	20.21	7.73	6.67	9.52	19.68	7.74	6.24	9.67
[Pt(MeBigH)(PPh ₃) ₂](HSO ₄) ₂	19.20	6.53	5.90	18.91	18.98	6.81	6.02	18.60
[Pt(Diet.Big)(PPh ₃) ₂](OH)	21.93	7.28	6.21	—	21.85	7.83	6.45	—
[Pt(Diet.BigH)(PPh ₃) ₂]Cl ₂	21.00	7.23	6.26	7.93	20.60	7.39	6.54	7.49
[Pt(Diet.BigH)(PPh ₃) ₂]SO ₄	20.81	6.98	6.16	9.38	20.08	7.20	6.38	9.88
[Pt(Diet.BigH)(PPh ₃) ₂](HSO ₄) ₂	18.25	6.13	5.46	18.20	18.19	6.53	5.79	17.94
[Pt(PhBig)(PPh ₃) ₂](OH)	21.5	7.53	6.41	—	21.38	7.67	6.79	—

Big = biguanide (C₂H₆N₅), Me.Big = methylbiguanide (C₃H₈N₅),
 Diet.Big = diethylbiguanide (C₆H₄N₅), Ph. Big = phenylbiguanide (C₈H₁₀N₅).

TABLE 2 — INFRARED SPECTRAL DATA OF THE COMPLEXES

PPh ₃	(BigH)(SO ₄) ₂	<i>cis</i> -[Pt(PPh ₃) ₂ Cl ₂]	<i>cis</i> [Pt(BigH)(PPh ₃) ₂ (OH) ₂]	<i>cis</i> [Pt(BigH)(PPh ₃) ₂ Cl ₂]	<i>cis</i> [Pt(BigH)(PPh ₃) ₂ SO ₄]	<i>cis</i> [Pt(BigH)(PPh ₃) ₂ I ₂]
—	3540	—	3440	3400	3420	3440
—	3290	—	3360	3340	3340	—
—	3170	—	3180	3140	3180	—
3060	—	3050	3050	3050	3050	3050
—	—	—	—	2915	—	2922
—	—	—	—	2812	—	2850
1755	1650	—	1620	1655	1658	1660
—	1640	—	—	1615	—	1610
1590	1560	1615	1560	1565	1582	1562
—	1525	—	1525	1525	1568	1512
—	1500	—	—	—	1532	1500
—	—	—	—	—	1520	—
1460	—	1474	1475	1475	1477	1473
—	—	1426	1435	1425	1435	1426
—	—	—	1432	—	1430	—
—	—	1305	1305	1305	1312	1300
1280	—	—	—	—	1280	—
1270	1230	—	—	1270	—	—
1205	—	—	—	—	—	—
1175	—	1178	1180	1180	1183	1178
—	—	—	—	—	—	1152
1160	1135	1080	1095	1090	1092	1087
1092	1120	—	—	—	1049	1038
1070	1075	—	—	—	—	—
1030	—	1020	1025	1015	—	1018
1000	980	990	997	997	997	990
—	—	—	846	953	967	—
935	—	—	—	910	958	—
980	—	—	—	840	850	—
765	740	744	748	735	745	732

stretch; and (iii) boiling the complex bases with conc. hydrochloric acid produces the original *cis*-Pt(PPh₃)₂Cl₂. If Ph₃PO is coordinated with Pt(II), the decomposition product should have contained the Ph₃PO as one of the products.

From the mode of preparation and high stability of *cis*-bis(triphenylphosphine)biguanidinium platinum (II), it may be concluded that the strong *trans*-effect of two triphenylphosphine groups at the *cis*-position of the platinum atom in *cis*-Pt(PPh₃)₂Cl₂ helps in the coordination of *cis*-orienting chelating ligand biguanide.

The metal biguanide chelates with delocalized π-electron system can be visualized as pseudo-aro-

matic compounds. Introduction of electron withdrawing group triphenylphosphine, on biguanide-platinum(II) ring can be compared to a similar aromatic system where an electron withdrawing group such as nitro group is attached to the benzene ring (cf *m*-nitroaniline). Since the attachment of phosphine to the platinum is likely to influence —NH₂ groups in the 3,5-positions, it was thought interesting to compare the mesomeric effect of nitro group in *m*-nitroaniline with that of triphenylphosphine in *cis*-[Pt(BigH)(PPh₃)₂]²⁺.

The IR spectra of the compounds have been recorded and the absorption bands are given in Table 2. In monoprotonated biguanide molecule,

very strong absorption is noticed at 3540 cm⁻¹ for ν_a NH₂. The simple bis(biguanidinium) metal(II) chlorides, [M(BigH)₂]Cl₂ (where M = Cu, Ni) show strong absorption at 3320 cm⁻¹ ascribable to ν_{as} NH₂. This indicates that the influence of conjugation in metal-biguanide ring is effective over the NH₂ group. The *cis*-bis(triphenylphosphine)biguanidiniumplatinum(II) exhibits two strong absorptions at 3440 and 3340 cm⁻¹ corresponding to two -NH₂ stretches. Again νNH for secondary amine group attached to the metal appears at 3140 and 3180 cm⁻¹ for the *cis*-bis(triphenylphosphine)biguanidiniumplatinum(II) complexes and this absorption for the secondary amines is evident only when it is attached to a strong electron withdrawing group (cf N',N'-diphenyldicyandiamide).

From a comparison of the -NH₂ stretches of *m*-nitroaniline and bis(triphenylphosphine)biguanidiniumplatinum(II), it can be inferred that π-electron delocalization over the biguanide-metal-phosphine complexes occurs and the strong π accepting characteristics of triphenylphosphine seems to be operative in this complex. A decrease in electron density in the biguanide ring of the *cis*-[Pt(BigH)(PPh₃)₂]²⁺ complex is expected and is observed from the lowering of ring C=N as well as C-N stretches (in C-NH₂) as given below:

Compound	Ring νC=N (cm ⁻¹)	νC-N (C-NH ₂) (cm ⁻¹)
Biguanide normal sulphate	1640(vs)	1650(vs)
Ni(BigH) ₂ Cl ₂	1605(vs)	1680(vs)
<i>cis</i> -[Pt(BigH)(PPh ₃) ₂](OH) ₂	1560(vs)	1620(vs)

The question of aromaticity of benzenoid resonance and hence ring-current of metal biguanide as well as the influence of metal *d*-orbital over triphenylphosphine arising from the participation of appropriate metal *d*-orbitals in *dπ-pπ* and *dπ-dπ* bonding with the ligands is of particular importance. The UV absorption spectra indicated the possibility of metal to participate in *dπ-pπ* overlap with the π-system of the chelate ring. The π-electron delocalization can explain the spectral as well as the chemical properties of metal biguanide complexes. In case of biguanide complexes, two maxima have been observed in the ultraviolet region, one at 230 nm (λ_{max2}) and the other at 200 nm (λ_{max1}). In the electronic spectra of *cis*-bis(triphenylphosphine)biguanidiniumplatinum(II) complexes, a sharp intense absorption (ε = 24720) is observed at 230 nm corresponding to λ_{max2}, but no absorption corresponding to λ_{max1} is noticed. In bis(biguanidinium)platinum(II) chloride, λ_{max2} is observed at 220 nm (ε = 29250) and λ_{max1} is absent. The strength of metal biguanide bonding in *cis*-bis(triphenylphosphine)biguanidiniumplatinum(II) can be understood from the comparison of its ε-value with that of bis(biguanidinium)platinum(II)

chloride. ε, the molar extinction coefficient, per biguanide is 24720 for the former and 14625 for the latter. The band at 232 nm has been assigned to the transition from the symmetric level to the antisymmetric level. For the bis(biguanidinium)platinum(II) and palladium(II), one band is observed and that is blue shifted (232 nm band for the free ligand is shifted to 220 nm) for the [Pt(BigH)₂Cl₂] which is explained on the basis of the energy level scheme². In these cases the *d*-orbital could be above the π-orbital and then both π₁-π₂ and π₁+π₂ will be stabilized by the interaction indicating a blue shift of 232 nm band.

In case of bis(triphenylphosphine)biguanidiniumplatinum(II) the bonding of π-accepting ligands (i.e. triphenylphosphine) with metal would cause the π-electron deficiency over the metal *d*-orbital resulting in the stabilization of *d*, even very near to but not below the π-orbital of the ligand biguanide and the interaction with *d* would destabilize both π₁-π₂ and π₁+π₂. This destabilization results in the symmetric-antisymmetric transition of the biguanide in the complex at a higher wavelength compared to one in the absence of π-accepting ligand, but still at a lower wavelength compared to free ligand.

On the other hand the bonding in biguanide, a π-excess ligand to the platinum made *d*-orbital rich with π-electron causing the destabilization of the metal *d*-orbital with respect to the state when there were no such ligands. This destabilization would raise the *d*, even above the π-orbital of triphenylphosphine. The interaction of *d* with π would stabilize π-orbital as a result π-π* transition for triphenylphosphine in the complex resulting in blue shift in the spectrum compared to the free ligand. In the present case the 262 nm band for the ligand⁹, PPh₃, has been shifted to 258 nm in the complex. It can hence be concluded that in these mixed chelate complexes, electron delocalization on metal biguanides influences the electron drift in metal phosphine system.

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