

Coordinate Bonding Properties of Complexes of Pyridine with Platinum(II) and Mercury(II) Chlorides

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In order to elucidate the properties of metal–pyridine coordination bonding comparatively, spectroscopic measurements and quantum chemical calculations have been performed for dichloroplatinum(II) and mercury(II) complexes. The extent of XPS shifts of pyridine nitrogen induced by coordination was larger for Pt(II) than for Hg(II) complexes, whereas the influences observed for the C-13 nmr shifts of the pyridine moiety were rather small. These tendencies were reasonably accounted for by the iterative extended Hückel MO method in terms of valence electron densities, atomic or bond populations, and MO correlation diagrams. The importance of the valence state ionization potentials of the metal orbitals is emphasized in characterizing the coordination bonding for transition and non-transition metals.

Introduction

Metal–pyridine complexes have been studied spectroscopically by using X-ray photoelectron,¹ ultra-violet,² visible reflectance,³ infra-red,^{4,5} and nuclear magnetic resonance⁶ in order to elucidate the molecular structures and/or the properties of the coordinate bonds. Quantum chemical interpretations were given on some experimental results.⁷ For example, the extended Hückel MO calculations were carried out for the paramagnetic Ni(II) and Co(II) pyridine complexes, where the pmr contact shifts were well interpreted in terms of a ($\sigma + \pi$) spin delocalization mechanism.⁸ However, diamagnetic metal–pyridine complexes have never been investigated from the quantum chemical viewpoints, although diamagnetic metal complexes with carbonyl,⁹ olefins,^{10,11} or alkyl ligands¹² were dealt with successfully.

In the present work, *trans*-[PtCl₂py₂] and HgCl₂py₂ are closely investigated by C-13 nmr and X-ray photoelectron spectroscopies, together with the iterative extended Hückel MO method. The C-13 chemical shifts of the pyridine moiety and the shifts in N(1s) electron

binding energies should reflect the calculated charge redistributions due to coordination.^{13,14} The valence state ionization potentials (VSIP) of Pt and Hg orbitals, adopted here as the input parameters, have been established to be reliable from the calculations on Pt(II) square planar complexes¹⁵ and organomercury compounds.^{16,17} It is examined in this calculation whether the characteristics of the coordinate bonds of the typical transition and non-transition metal pyridine complexes may associate with the definite difference between the values of VSIP of Pt and Hg atoms or not.

Experimental

Both *trans*-[PtCl₂py₂]¹⁸ and HgCl₂py₂¹⁹ were prepared and purified according to the usual methods.

Cmr spectra were recorded on a JEOL PS-100 spectrometer (25.2 MHz) by the proton decoupled CW method for the saturated solutions of acetone. A Mcpherson ESCA spectrometer was used to obtain X-ray photoelectron spectra, which were calibrated by the Au standard.

Calculations

Extended Hückel MO calculations were carried out by a Hitac 8700/8800 computer at the University of Tokyo. With regard to the input parameters of VSIP and the Slater exponents, the same values as reported^{15–17} were used. Calculations were converged on a charge iteration procedure at the sensitivity of 2.00 eV/charge.

The bond distances of the square-planar *trans*-[PtCl₂py₂] complex were set in reference to the structural data.²⁰ According to an X-ray analysis,²¹ the Hg atom of the complex, HgCl₂py₂, was in a distorted octahedral environment (similar to CuCl₂py₂), where two axial chlorine atoms were located at a very remote position of 3.25 Å and a square planar unit was constituted of both the other chlorine atoms (Hg–Cl = 2.34 Å) and the two pyridine ligands (Hg–N = 2.60 Å). In order to compare the Hg(II) complex with the Pt(II) complex, the remote two chlorine atoms were neglected and, con-

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sequently, the square-planar *trans*-geometry was adopted in this calculation. The pyridine part of the complexes was assumed to have the same geometry as pyridine molecule itself,²² since the small change of the geometry have little affected the calculated results.²³

Results

The carbon chemical shifts of pyridines, coordinated or uncoordinated, are summarized in Table I, together with the calculated valence electron densities of the corresponding carbons. With regard to the N(1s) binding energies, the observed values of coordinated pyridine were compared with that of the solid pyridine.²⁴ As shown in Table II, $E_b(1s)$ of pyridine nitrogen increased by coordination. The N(1s) binding energy is usually understood in terms of the net charge of nitrogen, obtained as the valence electron density minus 5.00. The higher shifts of the N(1s) binding energies indicate that the more negative charge of nitrogen is transferred to the metal atoms.

A correlation diagram in molecular orbitals concerning the pyridine coordination to these metal ions is

TABLE I. The Carbon-13 Chemical Shifts and the Valence Electron Densities of Pyridine Carbons.

Carbon Position	Compound	Chemical Shift (ppm) ^a	Valence Electron Density
2,6	Pt(II) Complex	154.9	3.78
	Hg(II) Complex	150.1	3.79
	Free Pyridine	150.2	3.78
4	Pt(II) Complex	143.8	3.93
	Hg(II) Complex	139.6	3.94
	Free Pyridine	135.9	3.93
3,5	Pt(II) Complex	127.8	3.99
	Hg(II) Complex	126.3	4.00
	Free Pyridine	123.9	4.00

^a Relative to TMS.

TABLE II. The 1s Binding Energies and the Valence Electron Densities of Pyridine Nitrogen.

Compound	$E_b(1s)$ (eV)	Valence Electron Density
Pt(II) Complex	402.2 (+ 4.2) ^a	5.26
Hg(II) Complex	399.3 (+ 1.3) ^a	5.54
Free Pyridine	398.0 (0.0) ^a	5.59

^a Shifts relative to free pyridine are given in parentheses.

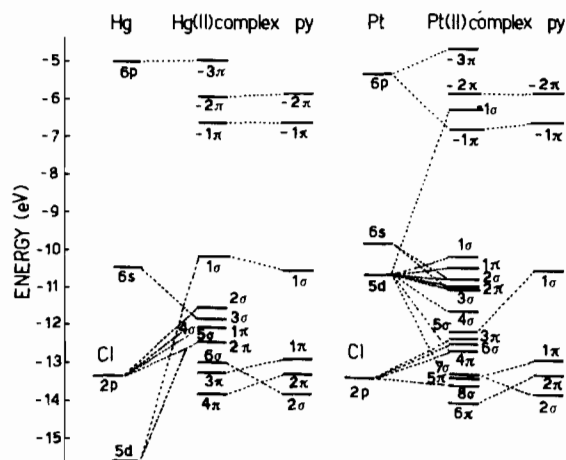


Figure 1. MO correlation diagrams for Hg(II) and Pt(II) pyridine complexes.

shown in Fig. 1. For each metal–pyridine complex, the molecular orbitals of the complexes are given at the center, while the valence ionization potentials of free atoms are drawn as the levels on the left side and the molecular orbitals of free pyridine on the right side. The π and σ symmetries with respect to the molecular plane of pyridine were designated by considering the s -orbital populations of its constituent atoms, whether all the values were zero or not. The occupied and unoccupied orbitals were discriminated by the signs of plus or minus, respectively. In addition, the integral numbers were given from the highest occupied or the lowest unoccupied orbitals as 1σ , 1π , 2π , ..., or -1π , -2π , -1σ ...

Orbital correlations were shown by dotted lines between the complex and free pyridine, judging from the signs and the magnitudes of the s - or p_z -orbital coeffi-

TABLE III. Metal–nitrogen Bond Populations and Their Metal Orbital Contents in Pyridine Complexes.

Compound	Total Bond Population	(%)		
		M(6s)	M(6p)	M(5d)
Pt(II) Complex	0.41	29.2	39.0	32.0
Hg(II) Complex	0.09	76.9	21.6	1.0

TABLE IV. Atomic Orbital Populations of Pyridine Nitrogen.

Compound	2s	2p _x	2p _y	2p _z
Pt(II) Complex	1.42	1.41	1.15	1.28
Hg(II) Complex	1.42	1.78	1.13	1.22
Free Pyridine	1.40	1.86	1.12	1.22

TABLE V. Atomic Orbital Populations of Metal in Pyridine Complexes.

Compound	6s	6p _x	6p _y	6p _z	5d _{xy}	5d _{yz}	5d _{zx}	5d _{z²}	5d _{x²-y²}
Pt(II) Complex	0.64	0.19	0.24	0.05	2.00	2.00	2.00	1.89	0.80
Hg(II) Complex	0.77	0.08	0.11	0.20	2.00	2.00	2.00	1.97	1.97

cients of nitrogen and five carbon atoms in the pyridine moiety. For example, the 1σ and 1π orbitals of free pyridine were correlated to the 1σ and 3π orbitals of the Hg(II) complex or the 5σ and 5π orbitals of the Pt(II) complex, respectively. Dotted lines were also used for the atomic orbitals of metals or chlorine, when the magnitudes of their orbital coefficients in the complexes were over 0.2 for metals or 0.5 for chlorine.

The iterated charges of metals in the complexes were + 0.22 (Pt) and + 1.07 (Hg), whereas those of chlorine were -0.48 and -0.53, respectively. The metal-nitrogen bond populations as well as their metal orbital contents are given in Table III. The atomic orbital populations of pyridine and of metals in the complexes are shown in Tables IV and V, respectively.

Discussion

It has been pointed out that the observed chemical shifts of azine carbons correlate well with the calculated valence electron densities.¹³ The main features of all sorts of the carbon shieldings are obviously explained by them, whether the pyridine moiety is coordinated or not (Table I).

With regard to the N(1s) binding energies, the larger the values of E_b(1s), the more positive the nitrogen charge (Table II). It is certain that the coordinated nitrogen atoms are stabilized by electron transfer to metal ions. Apparently, its extent is larger for Pt(II) and moderate for Hg(II), taking into consideration the increments of 0.9 eV for pyridine-ICl complex²⁵ and of 1.9 eV for ZnCl₂py₂.²⁶

The difference in strength of the metal-pyridine coordination is reasonably reproduced by the M-N bond populations, while the difference in bonding properties is characterized in the d-orbital participations; both of them are larger for Pt(II) than for Hg(II) (Table III). The atomic orbital populations of coordinated nitrogen are also different; the Hg(II) complex is more alike to free pyridine than the Pt(II) complex (Table IV). It is noteworthy in this connection, however, that the strength of HgCl₂-pyridine coordination should not be underestimated, as the adduct-forming enthalpy of 63.6 kJ/mol was reported.²⁷

As shown in Fig. 1, one of the unoccupied orbitals of the Pt(II) complex, *i.e.*, -1σ orbital, is correlated to the d orbital of the platinum atom. On the ground of its orbital coefficients, it has been ascertained that the

orbital is constituted mainly from platinum d_{x²-y²}, which is usually considered as vacant in a square-planar symmetry. The molecular orbital scheme of this complex is consistent with the electronic spectra.²⁸ This is assigned to be the inverse electron-transfer transition, *i.e.*, the highest occupied orbitals are constituted from the platinum d orbitals and the lowest unoccupied orbitals from the pyridine π orbitals. On the contrary, the mercury d orbitals are too low in energy to correlate with the pyridine valence orbitals, as revealed in the diagram of the Hg(II) complex.

The participation and delocalization of d orbitals in the Pt(II) complex are evident from the d_{x²-y²} and d_{z²} orbital populations, whereas all d orbitals in the Hg(II) complex are actually filled, indicating that the d electrons of mercury behave as if they were in an inner sub-shell (Table V). The two electron deficiency in the d orbitals of platinum, in contrast with mercury, is certainly helpful for the electron transfer from pyridine nitrogen.

It seems apparent that these features are caused by the difference in energy levels of metal d orbitals. The importance of energy-level matching between metals and ligands was previously suggested by Maitlis in order to characterize the series of metal π-complexes.²⁹ By inspecting the orbital energies of metal atoms and ligand molecules, it is possible to prospect the energy-level matching in orbital correlations to a certain extent, since the metal orbital energies in complexes deviate little from those in atoms under the restriction of charge neutrality. The participation and delocalization of d orbitals in these complexes, therefore, can be expected from the simple comparison of the proposed valence state ionization potentials of 5d electrons (Pt: 10.6, Hg: 15.7 eV) with the observed ionization potentials of gaseous pyridine (9.6, 9.8, 10.5 eV).³⁰

As for the platinum and mercury, the characteristics of the metals in the pyridine complexes are thus satisfactorily explained in terms of the VSIP values. As a matter of fact, the quantum chemical studies on the complexes are more direct than the simple comparison concerning the energy levels of its components, as far as the reliabilities of the atomic parameters are ensured beforehand.

The present approach will be very useful to elucidate the bonding properties of the complexes with common geometry and ligands, notwithstanding the number of d electrons. The coordination bonding with neutral ligands is especially suitable for consideration, since the spec-

troscopic investigations as well as quantum chemical ones are effectively accomplished concerning the influence of coordination on the physical properties.

Conclusion

(1) The nmr shifts of pyridine carbons and the XPS shifts of pyridine nitrogen are interpreted appropriately by the valence electron densities.

(2) The strength and bonding properties of Pt(II)– and Hg(II)–pyridine coordination are well analyzed in terms of various kinds of the populations.

(3) The contrast between these complexes are reproduced also in the molecular orbital correlation diagram.

(4) The features of *d*-orbital participations can be predicted by comparing the orbital energies of metal atoms with the ionization potentials of pyridine molecule.

(5) The present approach will be useful to elucidate the coordination bonding in the complexes with common and neutral ligands, notwithstanding the number of *d* electrons.

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