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The Nature of Bonding in PtC and PtN

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Abstract: The nature of bonding in the title compounds has been studied by using CASSCF and FOCI techniques. The ground states of PtC and PtN are found to be $^1\Sigma^+$ and $^2\Pi$ state arising primarily from:…$1\sigma^2 2\sigma^2 1\pi^4 1\delta^4 3\sigma^2$ and …$1\sigma^2 2\sigma^2 1\pi^4 1\delta^4 3\sigma^2 2\pi^1$ configuration respectively and both of which form triple bond (one σ, two π bonds), but the bond of PtC is much stronger than that of PtN.

Keywords: PtC and PtN, nature of bonding, molecular constants, CASSCF, FOCI.

The theoretical study of small molecules containing transition metal atoms is one of the most active areas in quantum chemistry[1]. Very extensive studies have been done on first and second row transition metal hydrides[2,3], oxides[4-6] and the transition metal dimers[7-9]. But theoretical studies on the third row transition metal compounds are more scarce.

Platinum is an important element for catalytic reactions, and the knowledge of the interaction between Pt and C/N atom is basic, but important for the understanding of such catalytic aspects. The spectroscopic investigation of PtC and PtN has been reported[10-13]. But there is no *ab initio* predictions reported for properties of PtC. Recently we have reported the studies on the nature of bonding in PtN by MCSCF method[14]. In the present work we describe the nature of the bonding in PtC and PtN through *ab initio* calculations by using CASSCF and FOCI techniques and calculate their molecular constants. And several low-lying states were also investigated to indentify the ground states of PtC and PtN.

Methods

The calculations were firstly carried out for the optimizations of the different states of PtC and PtN by using HF method, followed by the CASSCF optimization calculations. Then, the first order CI (FOCI) calculations were done to include the higher-order electronic correlation effects. The relativistic compact effective potential (RCEP) and its matching basis set[15] was used for Pt atom and for C and N atoms, 6-31G(d) basis set was used. The CASSCF active space consists of 14 /15 electrons and 10 orbitals for PtC/PtN resulting in one more thousands of spin configuration functions. The FOCI method included all configurations in the CASSCF plus configurations obtained by distribution of 13/14 electrons (for PtC/PtN) in the internal space and one electron in the orthogonal external space in all possible ways including up to one-to-two hundred thousands spin configuration functions. The calculations of at least six single points lying near equilibrium geometry within 0.005Å were performed to determine the molecular constants based on Morse's potential energy function. All calculations were performed with PC GAMESS 5.0[16] running on PII PC computer.

Results and Discussion

It is found from the calculations that the ground states of PtC and PtN are $^1\Sigma^+$ and $^2\Pi$ state arising primarily from: $\ldots1\sigma^2 2\sigma^2 1\pi^4 1\delta^4 3\sigma^2$ and $\ldots1\sigma^2 2\sigma^2 1\pi^4 1\delta^4 3\sigma^2 2\pi^1$ configuration respectively which agree with the optical spectra of PtC[13] and PtN[10]. The low-lying $^1\Pi$, $^3\Pi$ states of PtC have the same dominant configuration$\ldots1\sigma^2 2\sigma^2 1\pi^4 1\delta^4 3\sigma^1 2\pi^1$, and the quartet $^4\Sigma^-$ state of PtN has the dominant configuration$\ldots1\sigma^2 2\sigma^2 1\pi^4 1\delta^4 3\sigma^1 2\pi^2$. The calculated molecular constants are listed in **Table1**.

Table1 The calculated molecular constants of PtC and PtN and their experimental values[13,10]

			Re (Å)	De (eV)	Te (eV)	We (cm^{-1})	XeWe (cm^{-1})	B0 (cm^{-1})
PtC	$X^1\Sigma^+$	CASSCF	1.721	4.60	0.0	993.0	6.6	0.5031
		FOCI	1.713	5.03	0.0	1067.3	7.0	0.5075
		Expt.	1.68					0.5289
	$A^1\Pi$	CASSCF	1.825	2.49	2.14	741.1	6.9	0.4472
		FOCI	1.809	2.93	2.10	803.9	6.8	0.4554
		Expt.	1.77		2.29			0.4780
	$a^3\Pi$	CASSCF	1.782	2.99	1.61	817.7	6.9	0.4695
		FOCI	1.759	3.54	1.49	726.2	6.5	0.4816
		Expt.						
PtN	$X^2\Pi$	CASSCF	1.755	2.36	0.0	817.4	8.6	0.4219
		FOCI	1.735	2.86	0.0	945.2	9.6	0.4282
		Expt.	1.683			947.0	5.0	0.4557
	$a^4\Sigma^-$	CASSCF	1.847	1.91	0.45	636.8	6.1	0.3810
		FOCI	1.812	2.40	0.46	726.2	6.8	0.3930
		Expt.	1.702		0.37	901.0	8.0	0.4452

De is obtained from the dissociation limits for the processes: $PtC \rightarrow Pt(^3D)+C(^3P)$; $PtN \rightarrow Pt(^3D)+N(^4S)$.

The calculated molecular constants by the CASSCF method are agreeable with experimental values with the exception of the bond length and the dissociation energies. And the FOCI calculations significantly improved the bond length and the dissociation energy. But for the transition energy (Te), the calculated values at the both levels are very close and quite agreeable with the experimental values. This is reasonable because the electron correlation effects of different electronic states are cancelled at the same calculation level while the transition energy is calculated and also implies that the CASSCF method is a valuable tool to qualitatively describe the electronic states of the transition-metal-containing compounds. The $^3\Pi$ state of PtC and the $^4\Sigma^-$ state of PtN lie higher than the corresponding ground state only by 1.49 and 0.46eV(experimental value: 0.37eV) respectively at the FOCI level and this indicates a high density of low-lying molecular states for PtC and PtN. This is because the energy separation between Pt atomic states arising from the $5d^{10}$, $5d^{9}6s^{1}$ and $5d^{8}6s^{2}$ configurations is small and Pt atomic spin-orbital interaction is large ($\xi_{5d} \cong$ 4000cm^{-1})[17]. Therefore, the spin-orbit interaction must be considerated for the accurate theoretical calculations of the transition-metal-containing compounds, especially for the 5d-transition metals. This is the defect of this work.

Table2 The population analysis and orbital analysis of the valence orbitals of the ground state ($^{1}\Sigma^{+}$) of PtC from the nature molecular orbital (at FOCI level)

Orbital	Atomic population		Overlap population	Orbital analysis % Pt			C		Occupation number
	Pt	C	PtC	s	p	d	s	p	
1 σ	0.16	1.64	0.18	13	11	16	57	3	1.98
2 σ	0.59	0.80	0.54	16	7	38	12	27	1.93
3 σ	1.95	0.07	-0.02	26	14	51	4	5	2.00
4 σ	0.03	0.05	-0.01	27	5	31	12	25	0.07
1 π	2.60	0.85	0.38		7	60		33	3.83
2 π	0.07	0.14	-0.02		9	37		54	0.19
1 δ	4.00	0.00	0.00			100			4.00
Total	9.40	3.55	1.05						14.00

Table3 The population analysis and orbital analysis of the valence orbitals of the ground state ($^{2}\Pi$) of PtN from the nature molecular orbitals (at FOCI level)

Orbital	Atomic Population		Overlap population	Orbital analysis % Pt			C		Occupation number
	Pt	N	PtN	s	p	d	s	p	
1 σ	0.03	1.95	0.01	13	11	8	65	2	1.99
2 σ	0.61	1.00	0.32	17	7	37	7	31	1.93
3 σ	1.94	0.07	-0.02	23	6	61	6	4	1.99
4 σ	0.06	0.04	-0.02	27	7	32	12	22	0.08
1 π	2.45	1.18	0.18		3	64		33	3.81
2 π	0.37	0.87	-0.04		10	35		55	1.20
1 δ	4.00	0.00	0.00			100			4.00
Total	9.46	5.11	0.43						15.00

The population analysis and orbital analysis of the valence orbitals of PtC and PtN for the ground states from the nature molecular orbitals (at FOCI level) is presented in **Table 2** and **Table 3**. The 1σ orbital of the ground state of PtC and PtN is mainly composed of C (2s)/N (2s) and the 2σ orbital is composed of Pt (6s), Pt (5dσ)and C (2pσ)/N (2pσ). From the orbital analysis, it is expected that the hybridization of Pt(6s) and Pt(5d) occurs. The σ (sd+) hybrid orbital is polarized towards C or N atom and forms a strong bond. The 1π orbital is composed of Pt (5dπ) and C (pπ)/N (pπ). The composition of this orbital and population analysis is evidently suggestive of a strong π -bond formed between Pt and C/N. The 3σ orbital is predominantly composed of Pt σ (sd-) with C (pσ)/N (pσ) orbital making only small contribution, and the orbital occupation mainly coming from the electrons of Pt atom and the overlap population being negative indicates the 3σ orbital is something like an anti-bonding orbital. Compared with that of PtN, the overlap populations of 2σand 1π orbitals of PtC are much larger and it strongly demonstrates that the bonds formed between Pt and C is much stronger than that of PtN. The calculated dissociation energies of them also show the same results. This can be explained by the fact that the energy level of the valence orbitals of C atom is closer to Pt (5d) orbitals than that of N atom and, furthermore, one of the electrons in PtN occupies the anti-bonding 2π orbital, which also decreases the bonding strength of PtN.

The atomic orbital populations of the ground states of PtC and PtN (at FOCI level) are (Pt:$5d^{9.20}6s^{0.58}6p^{0.15}$; C:$2s^{1.89}2p^{2.18}$) and (Pt:$5d^{9.06}6s^{0.56}6p^{0.05}$; N:$2s^{2.04}2p^{3.28}$) respectively. The total gross populations indicate the transfer of electronic charge from Pt to C and N (0.07 and 0.32 electrons for PtC and PtN respectively). This demonstrates that PtC has the character of covalent bond and PtN has some character of ionic bond. The Pt (6s) populations in PtC and PtN are smaller than 1.0 and Pt (5d) populations are larger than 9.0, implying that the promotion of electrons from 6s to 5d orbitals occurs when the bond formed between Pt and C or N.

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