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Interactions of formaldehyde and its substituted derivatives with HCN: structure, stability and interaction

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Abstract

Twelve stable structures of the interactions of HCN with RCHO (R = H, F, Cl, Br, NH_2, CH_3) are located on the potential energy surface at the MP2/aug-cc-pVDZ level. Interaction energies including both ZPE and BSSE corrections range from -5.80 to -21.07 kJ.mol^{-1}. The result of SAPT analysis shows that the electrostatic component has mainly contributed to the stability of the complexes. It is remarkable that the most stable complex of HCHO···HCN is **P1-H$_b$** which has not been reported in the literature. The red-shifting hydrogen bonds of the C-H···O and N-H···N types are observed in the **P1-H$_b$**, **P1-CH$_3$**, **P1-NH$_2$** and **P2-NH$_2$** complexes. On the other hand, the C-H···N(O) blue-shifting hydrogen bonds are observed in the rest of complexes. The contraction of C-H bond and the blue shift of its stretching vibrational frequency are inversely proportional with its polarity in the isolated monomer.

Keywords. Hydrogen bond, interaction energy, RCHO, HCN, QTAIM, SAPT.

1. INTRODUCTION

The hydrogen bonds of C-H···O and C-H···N types play a crucial role in the supramolecular structures for life, such as DNA, RNA, protein…[1] The investigation into factors affecting the formation and the origin of hydrogen bonds as well as their stability in these structures is urgent [2-4]. The HCN is one of the important model molecules in the theoretical studies, especially in the complexes of transitional metals or metal ions [5-8]. As the previous investigation, the stable complexes of interaction between HCN and HCHO [8] were contributed by both C-H···O(N) hydrogen bond and Lewis acid-base interactions. To our best knowledge, complexes of interactions of HCN with RCHO (R = F, Cl, Br, CH_3, NH_2) have not been reported. Furthermore, this investigation isperformed to clarify the stable structure, the stability and the role of Lewis acid-base interactions and C-H···O and C-H···N hydrogen bonds in the complex stabilization. Moreover, in the present study, we use the modern analysis methods, such as QTAIM, SAPT and NBO, to thoroughly examine the monomers and their complexes [9, 10].

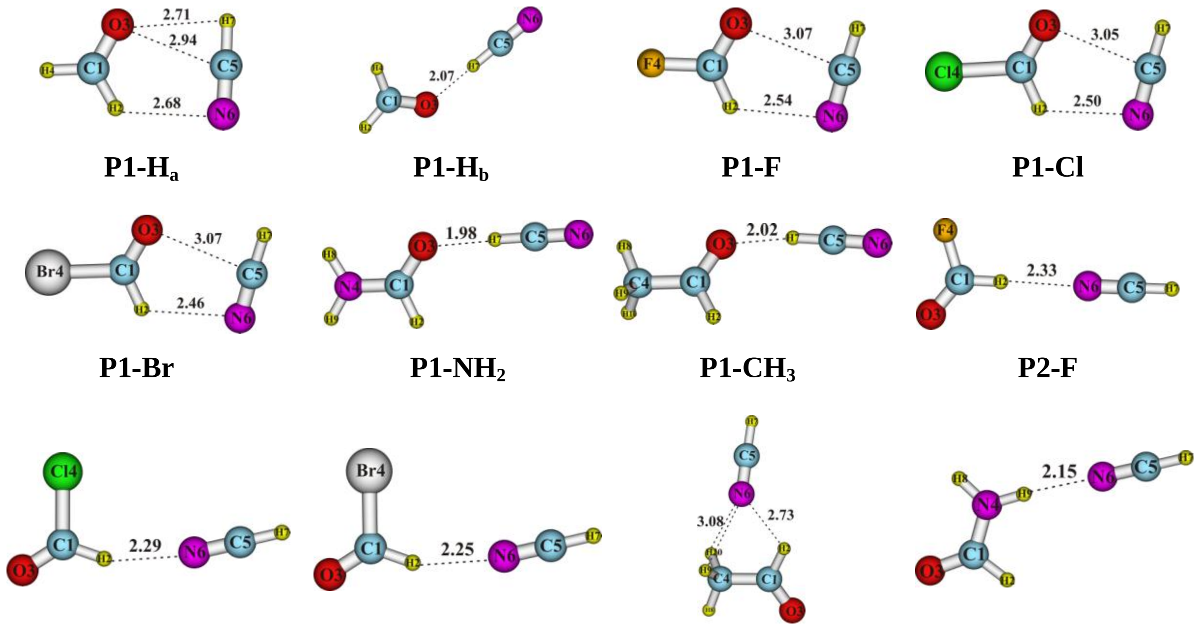
2. COMPUTATIONAL METHODS

All the stable structures of monomers and their complexes are optimized at the MP2/aug-cc-pVDZ level. Interaction energies are calculated at the CCSD(T)/aug-cc-pVDZ level with the geometric structures optimized at the MP2/aug-cc-pVDZ level. The interaction energy evaluated with only ZPE and both ZPE and BSEE corrections are symbolized with ΔE and ΔE*, respectively. The topological geometry, density of electron (ρ(r)), Laplacian of density ($\nabla(\rho(r))$) at the bond critical point (BCP) are estimated by using AIM2000 program [11]. The value of the total electron density transfer (EDT), s-character percentage (%s) and the electron density at the anti-bonding orbitals are estimated by means of NBO 5.G program [12]. The energy components contributing to the stability of the complexes, namely electrostatic attraction (E_{elest}), induction (E_{ind}), dispersion (E_{disp}), exchange (E_{exch}) and the second- and high-order level correlation ($\delta_{int,r}^{HF}$) terms are calculated by Psi4 program with SAPT2+ approach [13]. All other calculations are performed by Gaussian 09 (A.02) package [14].

3. RESULTS AND DISCUSSION

3.1. Geometric structures, interaction energies, changes of C-H and N-H bond length involved in hydrogen bond and their stretching vibrational frequencies

The interactions between HCN and RCHO (R = H, F, Cl, Br, CH_3, NH_2) induce twelve stable complexes with the C_s symmetry point group corresponding to two **P1** and **P2** shapes, presented in *Figure 1*. Particularly, **P1** shape refers to the complexes that have >C=O group involving in interactions, while the **P2** shape belongs to only C1-H2 (or N-H) covalent bond involved in interactions. Interaction energies (ΔE, ΔE*, $kJ.mol^{-1}$) at CCSD(T)/aug-cc-pVDZ//MP2/aug-cc-pVDZ are given in table 1. The changes of C(N)-H bond length (Δr, in Å), stretching vibrational frequency (Δν, in cm^{-1}) and its infrared intensity (ΔI, in $km.mol^{-1}$) at the MP2/aug-cc-pVDZ level, following complexation, are also given in the table 1.



P1-H_a **P1-H_b** **P1-F** **P1-Cl**

P1-Br **P1-NH_2** **P1-CH_3** **P2-F**

P2-Cl **P2-Br** **P2-CH_3** **P2-NH_2**

Figure 1: The optimized geometries of all complexes at the MP2/aug-cc-pVDZ level (distances in Å)

Table 1: Interaction energies and the changes of bond length, stretching vibrational frequency and infrared intensity of C-H or N-H covalent bonds involved in hydrogen bonds

Shape	R	ΔE	BSSE	ΔE*	Δr(C-H)	Δν(C-H)	ΔI(C-H)
P1	H_a	-14.06	3.35	-10.71	-0.0015	23.00	-45.53
					-0.0005(C5-H7)	*5.89*	*2.55*
	H_b	-17.32	4.21	-13.12	0.0073	-107.78	334.46
	F	-14.16	3.88	-10.28	-0.0002	6.18	-12.28
	Cl	-14.42	4.18	-10.23	-0.0005	10.06	-14.00
	Br	-14.88	4.85	-10.03	-0.0005	9.55	-13.55
	CH_3	-21.28	4.67	-16.61	0.0101	-172.56	564.94
	NH_2	-25.83	4.76	-21.07	0.0117	-150.99	464.31
P2	F	-14.18	3.97	-10.20	-0.0004	15.19	-1.52
	Cl	-14.68	4.67	-10.01	-0.0014	31.52	16.59
	Br	-15.57	5.33	-10.24	-0.0013	30.64	28.65
	CH_3	-9.53	3.73	-5.80	-0.0034	41.88	-22.33
					-0.0007(C4-H9(10))	*3.71*	*-1.04*
	NH_2	-17.58	4.34	-13.24	*0.0046 (N4-H9)*	*-36.85*	*125.40*

Table 2: Deprotonation energy (DPE) of C-H or N-H bonds involved in hydrogen bond and proton affinity (PA) at O (N) atoms at the CCSD(T)/aug-cc-pVDZ//MP2/aug-cc-pVDZ level (in kJ.mol^{-1})

Monomer	HCHO	FCHO	ClCHO	BrCHO	CH_3CHO	NH_2CHO	HCN
DPE(C(N)-H)	1681.9	1579.7	1530.4	1497.2	1654.3	1636.7(C); 1533.0(N)	1460.0
PA(O(N))	709.5	649.0	685.2	694.3	767.7	831.3	704.5(N)

As shown in figure 1, the intermolecular distances of O3···C5, H2(9)···N6 and H7···O3 contacts are in the range of 2.94-3.07 Å, 2.15-2.73 Å and 1.98-2.71 Å, respectively. All of them are smaller than the total of van der Waals radii of two atoms involved in these interactions (van der Waals radii of O, H, C, N atoms are in turn 1.52, 1.20, 1.70 and 1.55 Å). These values indicate the presence of hydrogen bonds and Lewis acid-base interactions upon complexation, namely H7···O3, H2(9)···N6 and O3···C5 contacts. It is noticeable that, in the **P2-CH$_3$** complex, the hydrogen bonds are formed between C4-H9(10)···N6 contacts in spite of their distance (*ca.* 3.08 Å) slightly larger than the sum of van der Waals radii of H and N atoms. This result should be assigned to the additional effect of the remaining interactions in the complex [15].

The interaction energies in the complexes considered are quite negative, which are in range from -9.53 to -25.83 with only ZPE correction and from -5.80 to -21.07 kJ.mol^{-1} with both ZPE + BSSE corrections. In particular, **P1-NH$_2$** is the most stable complex (ΔE^* = -21.07 kJ.mol^{-1}), while **P2-CH$_3$** is the least complex (ΔE^* = -5.08 kJ.mol^{-1}). It is remarkable that the **P1-H$_b$**, **P1-CH$_3$**, **P1-NH$_2$** and **P2-NH$_2$** complexes are more stable than the rest of complexes in spite of only one H···O(N) hydrogen bonding contact in each complex. Generally, interaction energies of the complexes decrease in the order of Br ≈ Cl ≈ F ≈ H_a < H_b < CH_3 < NH_2 derivatives (**P1** shape) and CH_3 < Cl ≈ F ≈ Br < NH_2 derivatives (**P2** shape). This trend is due to the change of DPE values of C-H, N-H bonds and PA at O and N sites in the isolated monomers that are involved in the hydrogen bond and Lewis acid-base interaction (*cf.* table 2).

The calculated results show that the DPE(C-H) (in HCN) < DPE(N-H) (in NH_2CHO) < DPE(C-H) (in RCHO). This means that the polarity decreases in the order of the C-H bond (HCN), to the N-H bond (NH_2CHO) and then to C-H bond (the other monomers). In addition, the PAs at O site in HCHO, CH_3CHO and NH_2CHO are larger than that at N site in HCN. As a result, the H···O intermolecular interaction is stronger than the H···N interaction upon complexation. The C-H···O and N-H···N hydrogen bonds are thus more stable than the C-H···N. Consequently, the **P1-H$_b$**, **P1-NH$_2$**, **P1-CH$_3$** and **P2-NH$_2$** complexes have the larger stability in comparision with the remaining complexes. In the **P1-H$_a$**, despite the existence of the C-H···O hydrogen bond, it is less stable than the complexes mentioned above. It should arise from the steric effect on interactions formed in complexes. In the following analyses we consider it more detailed.

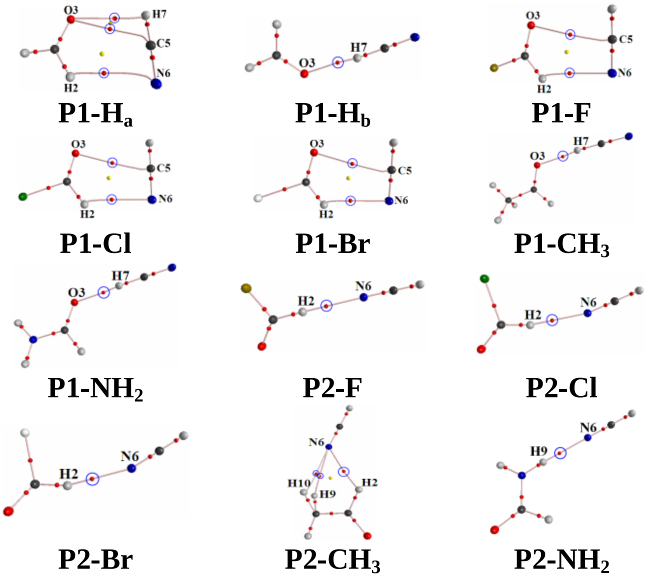
Following complexation, the replacement of one H atom in HCHO by halogen atoms (F, Cl, Br) causes an increase in strength of hydrogen bond and a decrease of strength of Lewis acid-base interaction.

Thus, DPE(C-H) decreases in the order: HCHO > FCHO > ClCHO > BrCHO, and PA(O) decreases in the order: HCHO > BrCHO > ClCHO > FCHO. As a consequence, the stability of halogenated derivatives' complexes is slightly different and approximates to the **P1-H$_a$** complex. The interaction energy calculated for **P1-H$_a$** complex is in a good agreement with that in the previous study [8]. Nevertheless, the most stable **P1-H$_b$** found in this present study is more stable than **P1-H$_a$**, which has not been reported in any literature.

In the cyclic and halogenated complexes, a contraction of C-H bond length compared to that in the relevant monomer, involved in hydrogen bonds, ranges from 0.0002 to 0.0034 Å, which is accompanied by an increase in the strectching vibrational frequencies and a decrease of the infrared intensities (see table 1). Our obtained results on changes of C-H bond length and its stretching vibrational frequency in HCHO···HCN are in a good agreement with the results reported in ref. [8]. Accordingly, these hydrogen bonds are classified as blue-shifting hydrogen bonds [2]. The blue shift of C-H distance is larger in **P1-H$_a$** than in **P1-X** (X = F, Cl, Br). The C-H blue shift is much larger for **P2-CH$_3$** than for **P2-X** (X = F, Cl, Br). The magnitude of C-H blue shift in these complexes is in line with the trend of polarity of C-H bond in the isolated monomers. Indeed, as shown in table 2, DPE(C-H) of CHO group in HCHO and CH_3CHO is much larger than that in XCHO (X = F, Cl, Br). The red-shifting hydrogen bond is observed in the **P1-H$_b$**, **P1-CH$_3$**, **P1-NH$_2$** and **P2-NH$_2$** complexes. It is remarkable that the C5-H7 red shift in the C5-H7···O3 hydrogen bond is larger than the N4-H5 red shift in the N4-H9···N6 hydrogen bond, which is due to both the larger PA at O sites in HCHO, CH_3CHO and NH_2CHO, and the larger polarity of C-H bond in HCN relative to PA at N site in HCN and the polarity of N4-H9 bond in NH_2CHO.

3.2. The AIM-, SAPT- and NBO-analyses

To more understand about the formation, strength and the nature of interactions in complexes, we performed the AIM analysis at the same level of theory, and results are illustrated in figure 2.



P1-H$_a$ **P1-H$_b$** **P1-F**

P1-Cl **P1-Br** **P1-CH$_3$**

P1-NH$_2$ **P2-F** **P2-Cl**

P2-Br **P2-CH$_3$** **P2-NH$_2$**

Figure 2: The topological geometry of the stable complexes at the MP2/aug-cc-pVDZ level

The obtained results indicate that there is existence of BCPs between O3···C5 and H···O(N) interactions with their corresponding electron density and Laplacian in the range of 0.0053-0.0232 au and 0.0161-0.0777 au. All of them fall within the critical limit for formation of weak interactions [16]. Thus, the O3···C5 and H···O(N) intermolecular interactions are Lewis acid-base interactions and hydrogen bonds, respectively. The electron densities at the H7···O3 and H9···N6 BCPs in the noncyclic complexes by *ca.* 0.0169-0.0232 au are significantly larger than those at BCPs of the other hydrogen bonded contacts and Lewis acid-base interactions in the rest of complexes (*ca.* 0.0053-0.0150 au). Therefore, the intermolecular interactions in the **P1-H$_b$**, **P1-CH$_3$**, **P1-NH$_2$** and **P2-NH$_2$** complexes are more stable than in the remaining complexes.

To gain further insight into the role of interactions to the complex stability, the energy components contributing to the stabilization energy are calculated using SAPT2+ approach at the aug-cc-pVDZ basis set and tabulated in Table 3. The SAPT energy (E_{SAPT}) is expressed as the sum of five terms as given below: $E_{SAPT} = E_{elest} + E_{ind} + E_{disp} + E_{exch} + \delta E_{int,r}^{HF}$ [9, 10], where E_{elest}, E_{ind}, E_{disp}, E_{exch} and $\delta_{int,r}^{HF}$ are electrostatic, induction, dispersion, exchange energy terms and the second- and high-order level correlation, respectively.

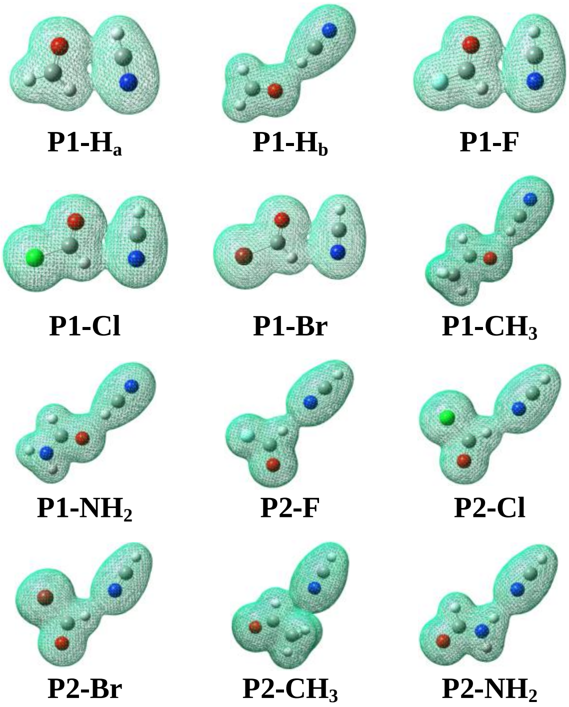
As shown in table 3, the electrostatic attraction term (E_{elest}) overcomes the other energy components, indicating a larger role of this force in stabilizing complex. In addition, the induction and dispersion energies also contribute to complexation strength. The interaction energies of complexes calculated using SAPT2+ approach (see table 3) are in a good agreement with the CCSD(T) method (see table 1). As a result, the **P1-H$_b$**, **P1-CH$_3$**, **P1-NH$_2$** and **P2-NH$_2$** complexes are more stable than the remaining complexes, and **P1-H$_b$** is more stable than **P1-H$_a$**.

Table 3: The energy components contributing to stability of complexes at the SAPT2+/aug-cc-pVDZ level (in kJ.mol^{-1})

Shape	R	E_{elest}	E_{ind}	E_{disp}	E_{exch}	$\delta E_{int,r}^{HF}$	E_{SAPT}
P1	H$_a$	-21.71	-8.56	-10.50	26.73	-2.33	-16.36
	H$_b$	-27.10	-9.66	-8.07	26.24	-3.51	-22.11
	F	-18.69	-7.12	-9.08	22.58	-1.71	-14.03
	Cl	-18.81	-7.83	-10.19	25.20	-2.05	-13.68
	Br	-18.60	-7.83	-10.40	25.55	-2.15	-13.43
	CH_3	-32.69	-12.70	-9.74	33.49	-4.73	-26.38
	NH_2	-39.34	-14.52	-10.53	38.09	-5.59	-31.90
P2	F	-18.92	-4.60	-6.04	15.41	-1.58	-15.73
	Cl	-18.91	-5.06	-6.73	16.53	-1.77	-15.94
	Br	-20.49	-6.37	-8.51	20.44	-2.17	-17.10
	CH_3	-9.48	-2.48	-6.31	8.74	-0.49	-10.01
	NH_2	-26.01	-7.85	-8.39	23.59	-2.47	-21.13

NBO analysis is performed for the monomers and their complexes, and the selected results are shown in figure 3 and table 4. The existence of Lewis acid-base interactions and hydrogen bonds as well as their stability in the complexes might be further understood by using iso-surface of complexes (see figure 3). It is clear that there is an overlap of electron density between monomers following complexation, implying the presence of the intermolecular contacts, including the hydrogen bond and Lewis acid-base interaction in the complexes.

Furthermore, as shown in table 4, the EDT values in the halogenated and in **P2-CH$_3$**, **P2-NH$_2$** complexes are negative, and in the rest of complexes those are positive. This means that for halogenated and **P2-CH$_3$**, **P2-NH$_2$** complexes, there is a transfer of electron density from HCN to RCHO, and inversely the electron density transfer occurs from RCHO to HCN in the rest of the complexes. A C-H bond contraction and a blue-shift of its stretching vibrational frequency in the C-H···N(O) hydrogen bond in **P1-F**, **P2-F**, **P2-Cl** and **P2-Br** complexes are determined by an increase of s-character percentage of C atom overcoming a slight increase of σ*(C-H) orbital. In **P1-H$_a$**, **P1-Cl**, **P1-Br** and **P2-CH$_3$** complexes, the blue-shifts depend on both an increase of s-character percentage of C atom and a decrease of σ*(C-H) electron density. On the other hand, an elongation of C-H and N-H bond involved in hydrogen bond, accompanied by a red-shift of their stretching vibrational frequencies, in the **P1-H$_b$**, **P1-CH$_3$**, **P1-NH$_2$** and **P2-NH$_2$** complexes is due to an increase of σ*(C-H) and σ*(N-H) electron density predominating over an increase of s-character percentage of C and N atoms following complexation.



P1-H$_a$ **P1-H$_b$** **P1-F**

P1-Cl **P1-Br** **P1-CH$_3$**

P1-NH$_2$ **P2-F** **P2-Cl**

P2-Br **P2-CH$_3$** **P2-NH$_2$**

Figure 3: The total electronic density for the complexes at the MP2/aug-cc-pVDZ level (*isovalue = 0.007 au/Å^3*)

Table 4: Selected results of NBO analysis at the MP2/aug-cc-pVDZ level

Shape	R	EDT (e)	Δσ*(C(N)-H) (e)	Δs(C/N) (%)
P1	H$_a$	0.0069	-0.0021	0.61
			-0.0002	0.43
	H$_b$	0.0226	0.0165	1.03
	F	-0.0014	0.0001	0.61
	Cl	-0.0012	-0.0002	0.68
	Br	-0.0015	-0.0002	0.75
	NH$_2$	0.0282	0.0210	1.37
	CH$_3$	0.0273	0.0202	1.18
P2	F	-0.0127	0.0018	1.34
	Cl	-0.0137	0.0006	1.96
	Br	-0.0141	0.0008	2.23
	CH$_3$	-0.0025	-0.0027	0.50
			0	0.09
	NH$_2$	-0.0143	0.0121	1.78

4. CONCLUSIONS

Interaction of HCN with RCHO (R = H, F, Cl, Br, CH_3, NH_2) induces twelve stable complexes with the interaction energy in the range of -5.80 and -21.07 kJ.mol^{-1} at the CCSD(T)/aug-cc-pVDZ//MP2/aug-cc-pVDZ level. Their stability is contributed by both Lewis acid-base interaction and C-H···N(O) hydrogen bond. It is remarkable that the most stable **P1-H$_b$** complex of HCHO···HCN has been repoted for the first time. The SAPT analysis indicates that electrostatic energy overcoming the induction and dispersion energies plays an important role in the stabilization of complexes.

The red-shifting hydrogen bonds are observed in **the P1-NH$_2$**, **P2-NH$_2$**, **P1-CH$_3$** and **P1-H$_a$** complexes. Remarkably, the red shift of C-H bond is larger than that of N-H bond in these complexes. On the contrary, the C-H···N(O) blue-shifting hydrogen bonds are found in the rest of complexes. The C-H blue shifts in these hydrogen bonds are inversely proportional to the C-H polarity in the isolated monomer. NBO analysis is also performed carefully to clarify the role of changes of σ*(C-H) and σ*(N-H) electron density and s-character percentage of C and N hybrid orbital on type of hydrogen bond in the complexes examined.

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