Electronic Supplementary Material (ESI) for Physical Chemistry Chemical Physics.

Supplementary Information

Anion-Anion and Anion-Neutral Triel Bonds

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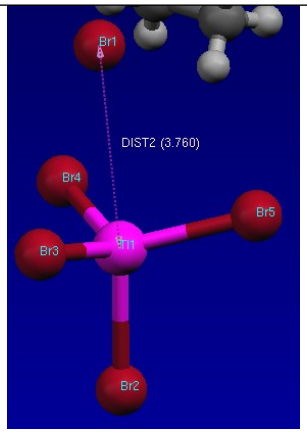	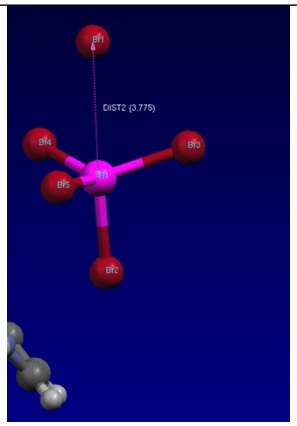
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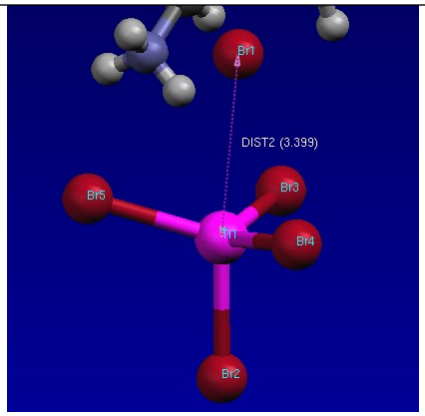	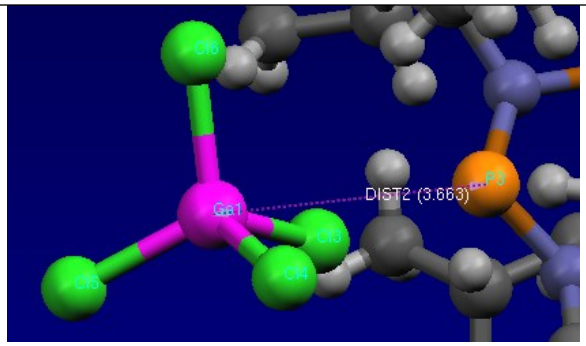
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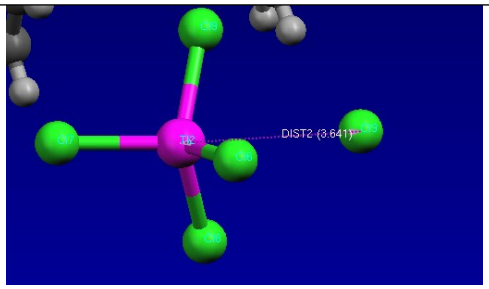	
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Fig S1. Five structures with refcodes from the CSD which appear to combine a TrX_4^- anion with a noncovalent triel bond.

Table S1. Internal bond lengths (Å) of tetrahedral $TrCl_4^-$ monomers calculated at the MP2/aug-cc-pVDZ level

	gas phase	aqueous
$AlCl_4^-$	2.197	2.192
$GaCl_4^-$	2.225	2.220
$InCl_4^-$	2.415	2.412
$TlCl_4^-$	2.474	2.471

Table S2. Higher energy of E relative to A geometries in aqueous solution, as measured by electronic and Gibbs free energies (ΔE_{el} and ΔG, in kcal/mol)

	E_{el}	G(298 K)
$NC^-\cdots AlCl_4^-$	4.23	3.05
$NC^-\cdots GaCl_4^-$	3.16	2.86
$NC^-\cdots InCl_4^-$	2.14	2.14
$NC^-\cdots TlCl_4^-$	1.23	1.96

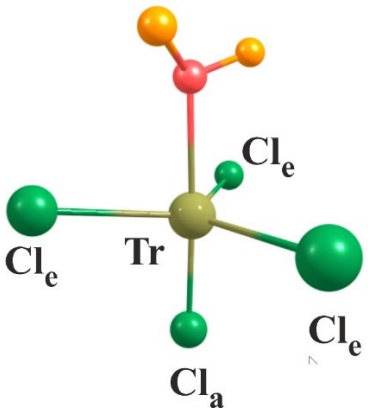


Fig. S2. The structures of $H_2O\cdots TrCl_4^-$ complexes.

Table S3. Interaction E_{int} and binding energy E_b of $H_2O\cdots TrCl_4^-$ complexes in water, all in kcal/mol.

	E_{int}		E_b	
	MP2	CCSD(T)	MP2	CCSD(T)
$H_2O\cdots AlCl_4^-$	-11.39	-10.39	1.46	2.24
$H_2O\cdots GaCl_4^-$	-5.27	-7.60	3.55	4.23
$H_2O\cdots InCl_4^-$	-9.28	-8.45	-3.51	-2.85
$H_2O\cdots TlCl_4^-$	-4.70	-3.98	-1.48	-0.96

Table S4. Structural parameters (distances in Å, angles in degs) for A complexes of $H_2O\cdots TrCl_4^-$.

	r(O···Tr)	r(Tr-Cl_a)	r(Tr-Cl_e)	θ(O···Tr-Cl_e)
	aqueous			
$H_2O\cdots AlCl_4^-$	2.115	2.295	2.232 2.231 2.230	87.2 82.8
$H_2O\cdots GaCl_4^-$	2.311	2.314	2.251 2.236	84.3 81.7
$H_2O\cdots InCl_4^-$	2.389	2.484	2.442 2.426	85.7 80.8
$H_2O\cdots TlCl_4^-$	2.568	2.542	2.486 2.472	84.5 79.2

Table S5. Deformation energies required to distort monomers from equilibrium geometry to that adopted within complex, all in kcal/mol.

	$TrCl_4^-$	NH_3	total
	A gas phase		
$H_3N\cdots AlCl_4^-$	12.83	0.24	13.07
$H_3N\cdots GaCl_4^-$	10.99	0.32	11.31
$H_3N\cdots InCl_4^-$	6.20	0.28	6.48
$H_3N\cdots TlCl_4^-$	5.05	0.55	5.60
	A aqueous		
$H_3N\cdots AlCl_4^-$	17.53	0.04	17.57
$H_3N\cdots GaCl_4^-$	16.23	0.07	16.30
$H_3N\cdots InCl_4^-$	9.77	0.06	9.83
$H_3N\cdots TlCl_4^-$	7.85	0.12	7.97
	E aqueous		
$H_3N\cdots AlCl_4^-$	33.08	0.14	33.22
$H_3N\cdots GaCl_4^-$	32.13	0.20	32.33
$H_3N\cdots InCl_4^-$	19.11	0.13	19.24
$H_3N\cdots TlCl_4^-$	15.83	0.23	16.06

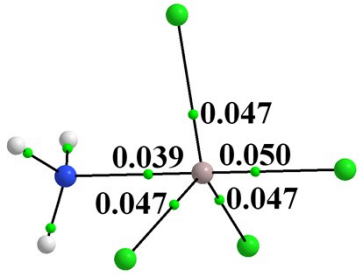
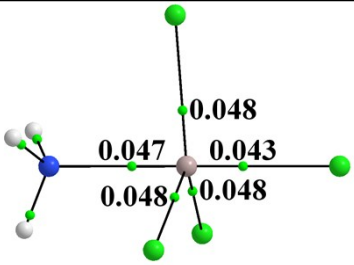
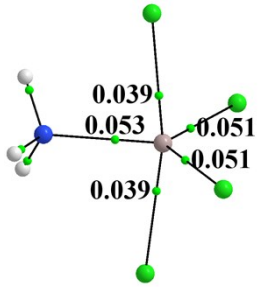
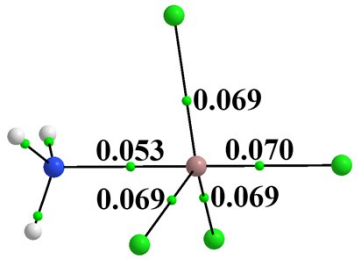
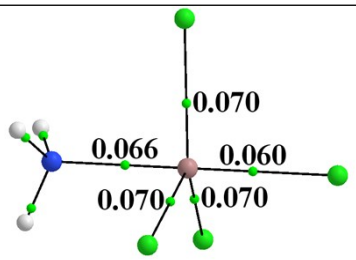
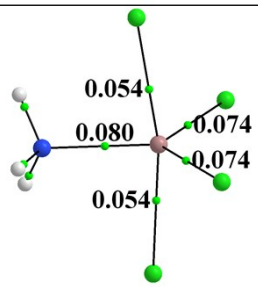
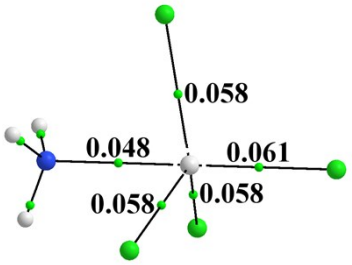
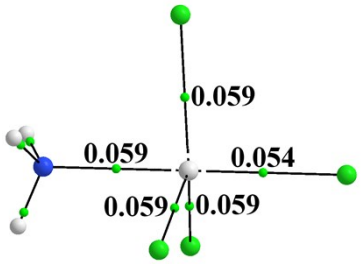
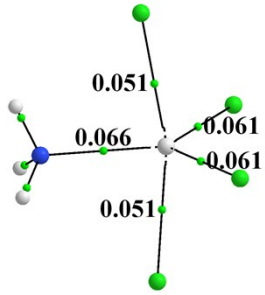
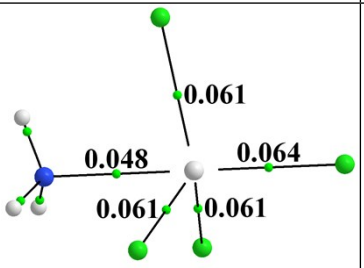
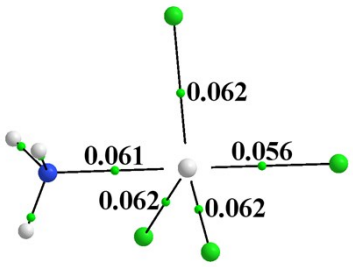
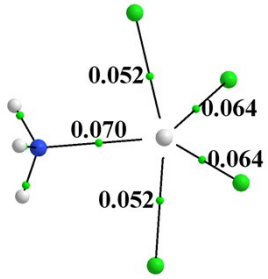
	A gas phase	A aqueous	E aqueous
$H_3N\cdots AlCl_4^-$			
$H_3N\cdots GaCl_4^-$			
$H_3N\cdots InCl_4^-$			
$H_3N\cdots TlCl_4^-$			

Fig. S3. AIM molecular diagrams of $H_3N\cdots TrCl_4^-$ complexes. Green dots represent bond critical points and the numbers refer to electron density at each bond critical point (in au)

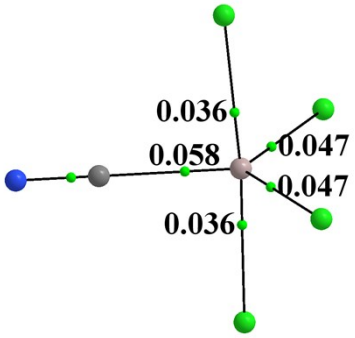
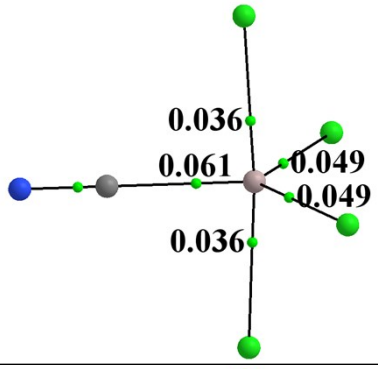
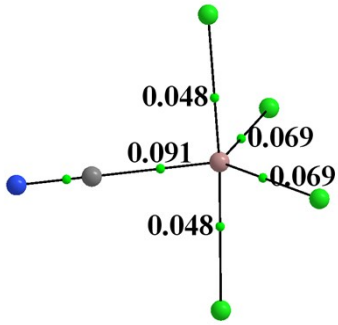
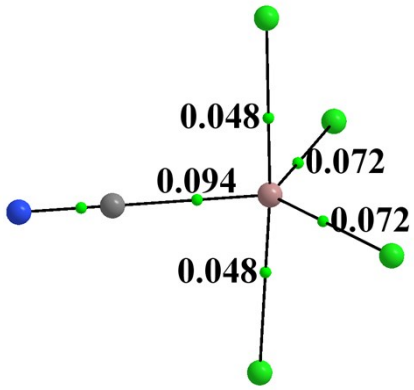
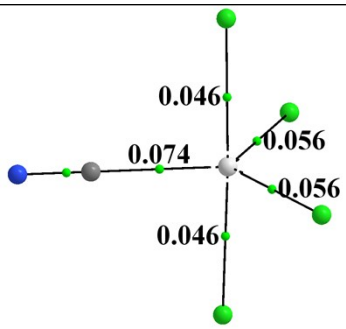
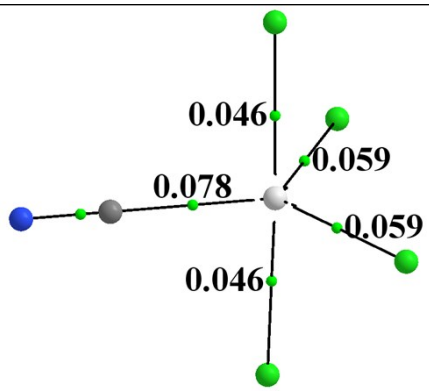
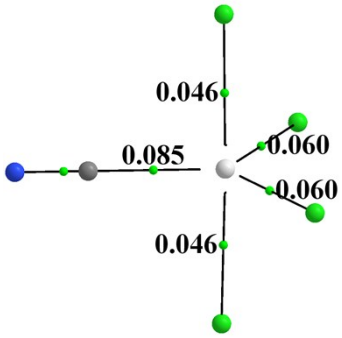
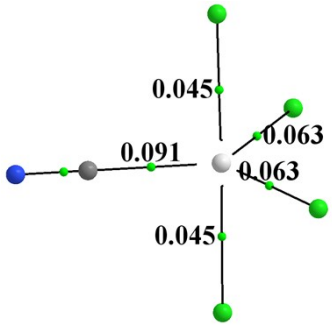
Table S6. Electronic and Gibbs free energies (ΔE_{el} and ΔG, in kcal/mol)[a] of configurations of $NC^-\cdots TrCl_4^-$ relative to E configuration.

	A	A'	E'
	gas phase		
$NC^-\cdots AlCl_4^-$	-0.24 (-0.15)	2.03 (2.13)	3.54 (3.44)
$NC^-\cdots GaCl_4^-$	1.08 (1.08)	5.85 (5.79)	7.06 (6.86)
$NC^-\cdots InCl_4^-$	0.20 (0.21)	5.05 (4.93)	6.15 (5.91)
$NC^-\cdots TlCl_4^-$	0.61 (0.59)	8.35 (8.11)	9.06 (8.78)
	aqueous		
$CN^-\cdots AlCl_4^-$	-0.02 (0.11)	2.49 (2.62)	3.95 (3.63)
$CN^-\cdots GaCl_4^-$	1.68 (1.63)	6.59 (6.46)	7.68 (7.36)
$CN^-\cdots InCl_4^-$	0.94 (0.62)	5.92 (5.49)	6.83 (6.34)
$CN^-\cdots TlCl_4^-$	2.01 (1.81)	9.68 (9.28)	10.26 (9.81)

[a] Gibbs free energies at 298 K in parentheses

Table S7. Deformation energies (E_{def}, kcal/mol) of $NC^-\cdots TrCl_4^-$

	gas phase			aqueous solution		
	$TrCl_4^-$	CN^-	total	$TrCl_4^-$	CN^-	total
E						
$NC^-\cdots AlCl_4^-$	47.14	0.15	47.29	40.30	0.12	40.42
$NC^-\cdots GaCl_4^-$	47.04	0.18	47.22	41.09	0.15	41.24
$NC^-\cdots InCl_4^-$	36.12	0.15	36.27	27.35	0.13	27.48
$NC^-\cdots TlCl_4^-$	32.64	0.16	32.80	26.36	0.13	26.49
A						
$NC^-\cdots AlCl_4^-$	31.85	0.10	32.05	25.58	0.07	25.65
$NC^-\cdots GaCl_4^-$	31.99	0.12	32.11	25.85	0.08	25.93
$NC^-\cdots InCl_4^-$	25.19	0.11	25.30	17.55	0.07	17.62
$NC^-\cdots TlCl_4^-$	23.82	0.13	23.95	16.87	0.09	16.96

	gas phase	aqueous solution
E		
$NC^{-}\cdots AlCl_4^{-}$		
$NC^{-}\cdots GaCl_4^{-}$		
$NC^{-}\cdots InCl_4^{-}$		
$NC^{-}\cdots TlCl_4^{-}$		
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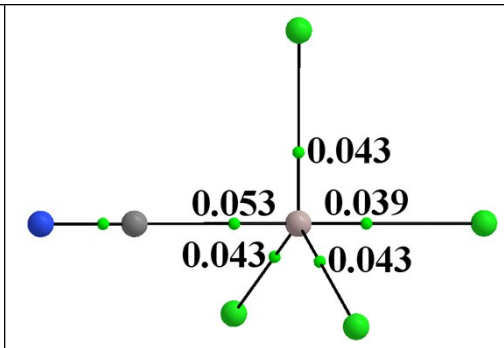
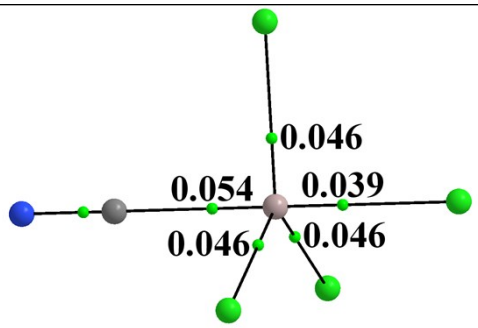
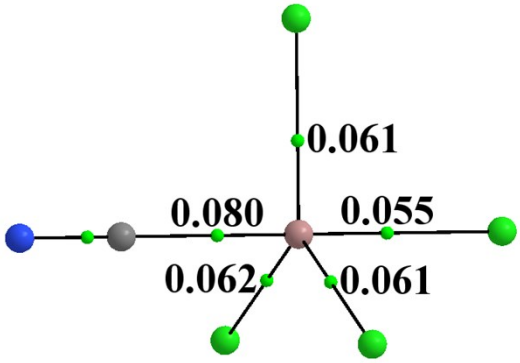
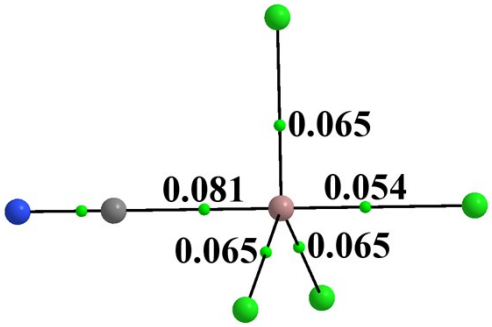
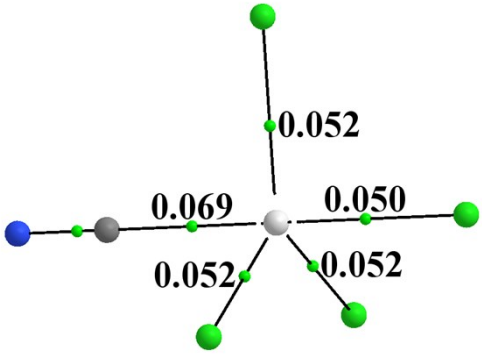
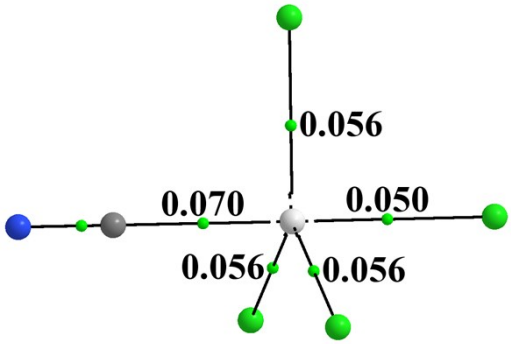
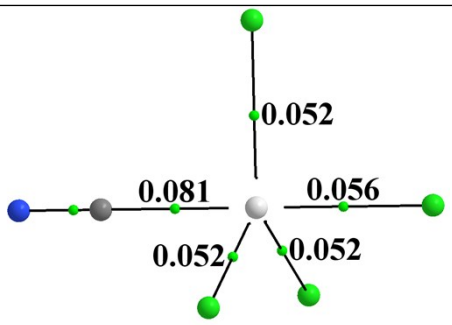
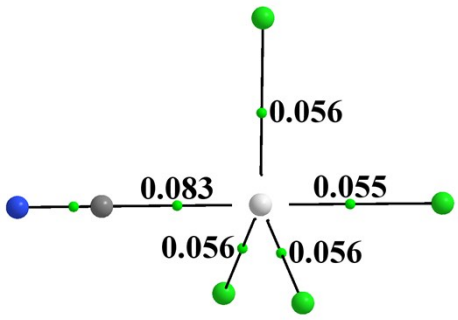
$NC^{-}\cdots AlCl_4^{-}$		
$NC^{-}\cdots GaCl_4^{-}$		
$NC^{-}\cdots InCl_4^{-}$		
$NC^{-}\cdots TlCl_4^{-}$		

Fig. S4. AIM molecular diagrams of $NC^{-}\cdots TrCl_4^{-}$ complexes. Green dots represent bond critical points. Numbers refers to electron densities at BCPs (in au)

Table S8. Thermochemical parameters of $H_3N\cdots TrCl_4^-$ complexes at 298 K. ΔH and ΔG in kcal/mol, ΔS in cal/K mole.

	ΔH	ΔS	ΔG
		A gas phase	
$H_3N\cdots AlCl_4^-$	-3.90	-37.27	7.21
$H_3N\cdots GaCl_4^-$	-2.74	-36.16	8.04
$H_3N\cdots InCl_4^-$	-8.40	-32.87	1.40
$H_3N\cdots TlCl_4^-$	-7.05	-32.26	2.57
		A aqueous	
$H_3N\cdots AlCl_4^-$	-10.92	-37.51	0.26
$H_3N\cdots GaCl_4^-$	-9.40	-36.92	1.61
$H_3N\cdots InCl_4^-$	-15.08	-34.58	-4.77
$H_3N\cdots TlCl_4^-$	-12.75	-33.59	-2.74
		E aqueous	
$H_3N\cdots AlCl_4^-$	-6.73	-33.70	3.32
$H_3N\cdots GaCl_4^-$	-6.14	-35.60	4.47
$H_3N\cdots InCl_4^-$	-12.83	-34.23	-2.62
$H_3N\cdots TlCl_4^-$	-11.38	-35.54	-0.78

Table S9. Thermochemical parameters of CN-···TrCl4- complexes at 298 K. ΔH and ΔG in kcal/mol, ΔS in cal/K mole.

	ΔH	ΔS	ΔG	ΔH	ΔS	ΔG
	E gas			E aqua		
$NC^-\cdots AlCl_4^-$	45.70	-32.22	55.31	-12.16	-32.29	-2.53
$NC^-\cdots GaCl_4^-$	43.77	-32.03	53.32	-13.86	-32.21	-4.26
$NC^-\cdots InCl_4^-$	32.95	-31.45	42.33	-21.06	-33.10	-11.19
$NC^-\cdots TlCl_4^-$	31.46	-31.10	40.73	-21.90	-32.12	-12.32
	A gas			A aqua		
$NC^-\cdots AlCl_4^-$	45.44	-32.57	55.15	-12.19	-32.74	-2.43
$NC^-\cdots GaCl_4^-$	44.81	-32.13	54.39	-12.22	-32.17	-2.63
$NC^-\cdots InCl_4^-$	33.14	-31.53	42.54	-20.14	-32.08	-10.58
$NC^-\cdots TlCl_4^-$	32.06	-31.09	41.33	-19.92	-31.56	-10.51

Table S10. Interaction energies (E_{int}, kcal/mol) and binding energy E_b (kcal/mol) of $H_3N\cdots TrCl_4^-$ complexes calculated at the M06-2X/def2tzvpp level in the gas phase.

	E_{int}	E_b
$H_3N\cdots AlCl_4^-$	-16.30	-1.45
$H_3N\cdots GaCl_4^-$	-10.42	0.19
$H_3N\cdots InCl_4^-$	-14.50	-7.21
$H_3N\cdots TlCl_4^-$	-9.62	-5.03