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The Structure of Pseudohalides—The Existence of a New Isomer

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Abstract: The pseudohalides MNCO, MNCS, and MN_3 (M = Li, BeH, BH_2, Na, MgH, AlH_2) were investigated by ab initio calculations, and a new isomer with a four-membered planar cyclic structure was found. The stabilities and isomerization barriers were calculated for these molecules. Three of them, NaNCS, LiNCS, and NaN_3, are possible candidates for future experimental investigations.

Introduction

Due to their varied structures, inorganic pseudohalides are often used as model compounds for the study of different physicochemical effects. They can have bent or linear, rigid or flexible frames, depending on the pseudohalide group and the nature of the substituents. An unusually high percentage of them is subject to low-frequency, large-amplitude motions.[1–8]

There are a number of possible pseudohalide isomers[9] with differing stabilities in the vapor phase. For the molecules with a sum formula CHNO, for example, there are 38 topologically different isomers, the most important of these being the cyanate, isocyanate, fulminate, nitrile oxide, oxazirine, and carbonitrene.[10] The substitution of the atoms of the pseudohalide group again provides many related molecules with sometimes quite different properties.

We recently performed ab initio calculations on a number of pseudohalide systems[1–8] and studied the large-amplitude bending motion by following the bending normal coordinate and calculating the optimum geometry with respect to all other coordinates.[3,6] For beryllium pseudohalides, an interesting effect was observed:[8] new T-shaped isomers were found for the thiocyanate and the azide. In these, the beryllium atom is bonded to the two end-atoms of the pseudohalide group, which is bent and forms a four-membered ring with the substituent atom. Similar structures were found by calculations by Schleyer et al. for the molecules C_3H_3Li and C_3H_3BeH[11] using small basis set ab initio calculations (HF/3-21G). We called these molecules "π-complexes" because they are stabilized by the interaction between the nonbonding orbitals of the pseudohalide π-system and the empty beryllium p-orbital of appropriate symmetry. However, both of these new complexes have an isomerization barrier of less than 200 cm^{-1}, even without considering the zero-point motion. Thus these are of little practical importance, unless studied in a free-jet expansion. The question then arose: Are there any π-complexes with high bonding energies, perhaps with stabilities similar to those of the "conventional" isomers, thus opening up the possibility to characterize them experimentally. The aim of this work was to provide an answer to this question.

Calculations

Calculations in this work were carried out by the Gaussian-92[12] and CADPAC[13] quantum chemical packages. They were performed either with a standard 6-31G**[14,15] or a TZ2P[16,17] basis set, where the polarization functions for the latter basis were taken from refs 18 and 19. The *d*-functions on lithium were 0.2 and 0.9, on sodium 0.084 and 0.332. Correlation energy was allowed for using second- and fourth-order Møller–Plesset perturbation theory (MP2 and MP4).

All geometry optimizations were performed at the MP2 level using the gradient method, where the largest gradient at the end of the optimizations was less than 10^{-5} au. Harmonic vibrational frequencies were calculated at the equilibrium geometry to ensure that these geometries were real minima. Potential energy curves were determined by proceeding along the given reaction coordinate and optimizing all remaining degrees of freedom.

Results and Discussion

In this work, different pseudohalides, thought to be promising for π-complex formation, were investigated by ab initio calculations. As an empty p-orbital of the ligand atom was believed to be important for the bonding in these molecules, the six first- and second-row atoms Li, Be, B, Na, Mg, and Al were tried as possible ligands. Three possible functional groups were looked at: -NCO, -NCS, and $-N_3$. In our calculations, we have found 13 π-complexes, as shown in Table 1. Their stabilities are also given by their total energies relative to the most stable form and

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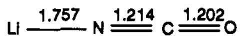
the respective isomerization barriers. All π-complex structures were located by obtaining their potential energy function with respect to the ligand group moving from one end of the pseudohalide group to the other, with the geometry of the rest of the molecule being optimized simultaneously. It must be noted that, apart from the π-complexes, this treatment provides information on only the lowest energy isomers of these molecules, i.e., the cyanate and isocyanate, the thiocyanate and isothiocyanate, and the azide. However, the other possible isomers are expected to be over 300 kJ/mol less stable[9] and thus require little attention.

From the first-row elements of interest, lithium forms a π-complex in all three cases with -NCO, -NCS, and -N_3 substitutions. The linear isocyanate **1** is the minimum energy form, but the π-complex **2** is still lower in energy than the cyanate **3**. The isomerization barrier in $\mathrm{LiN_3}$ (**4**) is somewhat higher. The situation for the thio compound is more surprising (see Figure 1): the π-complex **5** is the global minimum on the potential energy surface. The equilibrium isomerization barrier is ~15 kJ/mol between the isothiocyanate **6** and the π-complex. A further interesting feature of this class of compounds is that the thiocyanate does not exist, although the inflection point on the potential energy curve at an LiNC angle of ~40° indicates the likely shape of the molecule if it existed. From all classes of compounds we have investigated so far [e.g., **1**–**8**], this is the first molecule for which this isomer is not a stable form.



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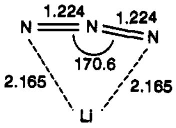

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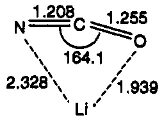

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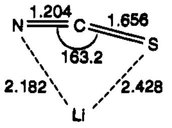

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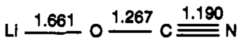

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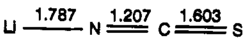

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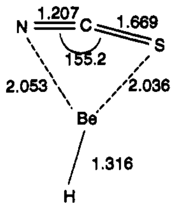
The π-complex formation for the ligand beryllium was already studied:[8] BeNCS (**7**) and $\mathrm{BeN_3}$ (**8**) were both found to be forming such a complex but with small izomerization barriers and high relative energies. A similar situation was encountered in this work for the studied boron-containing molecules: $\mathrm{BH_2NCS}$ (**9**) and $\mathrm{BH_2N_3}$ (**10**) also form π-complexes, which are barely stable.



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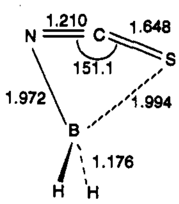

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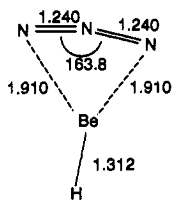

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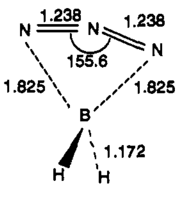

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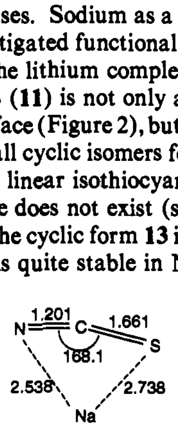
The situation is somewhat different for the studied second-row elements because of the increased readiness to form π-complexes in many cases. Sodium as a ligand forms π-complexes with the three investigated functional groups, the trends being similar to those for the lithium complexes (see Table 1). The π-complex of NaNCS (**11**) is not only a global minimum on the potential energy surface (Figure 2), but it also has the highest isomerization barrier of all cyclic isomers found so far by calculations (18 kJ/mol). The linear isothiocyanate **12** is rather unstable, and the thiocyanate does not exist (see inflection point at ~40°). For NaNCO, the cyclic form **13** is less stable than the linear, but the new form is quite stable in $\mathrm{NaN_3}$ (**14**).



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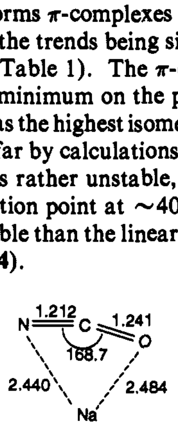

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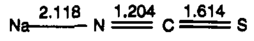

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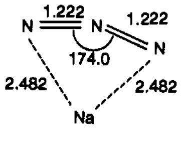

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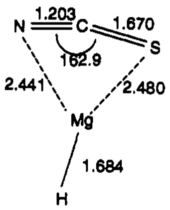
In magnesium, only the thio compound forms a π-complex (**15**). In case of aluminum as a ligand and the -NCS group, the thiocyanate **17** and the π-complex **18** both exist and have similarly shaped wells and similar total energies, with the linear form **19** being the most stable. The azide can also exist in the cyclic form (**20**).



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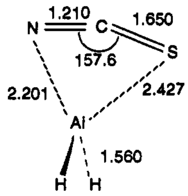

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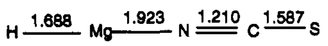

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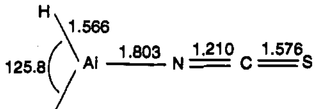

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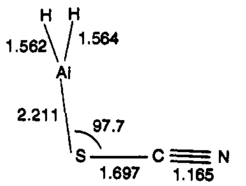

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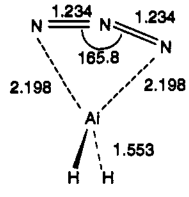

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To summarize, the majority of the above molecules (with the exception of some -NCO compounds and $\mathrm{HMgN_3}$) form π-complexes. The structure and bonding in all these molecules is rather similar: it can be described by the interaction of an empty p-orbital of the ligand atom with the pseudohalide π-system (see Figure 3). Probably the most characteristic feature of these molecules is the bent pseudohalide group (150–170°). The angle within this moiety decreases in higher groups of the periods of the periodic system. This can be explained by the fact that ligands with higher electronegativity have smaller p-orbitals, which can only achieve good overlap with the π-orbitals at smaller angles

Table 1. Structure and Stability of Different Pseudohalide π-Complexes[a]

π-complex molecule (no.[b])	X–B (Å)	A–B–C (deg)	total energy (au)	relative energy[c] (kJ/mol)	barrier[d] (kJ/mol)
LiNCO (**2**)	2.328	164.1	175.148 49	45.0	0.8
LiN_3 (**4**)	1.889	170.6	−171.277 89	27.5	4.6
	(1.844)	(168.3)	(−171.489 30)	(25.6)	
LiNCS (**5**)	2.016	163.2	−497.763 13	−0.66	14.6
	(1.975)	(164.6)	(−497.967 64)	(1.0)	(13.3)
			[−498.011 23]	[−5.19]	
BeHNCS (**7**)	1.802	155.2	−505.528 81	91.1	6.4
$BeHN_3$ (**8**)	1.638	163.8	−179.037 78	135.4	1.7
BH_2NCS (**9**)	1.780	151.1	−516.161 31	127.3	2.3
BH_2N_3 (**10**)	1.627	155.6	−189.676 34	173.0	0.5
NaNCS (**11**)	2.215	163.1	−652.158 23	−17.0	18.0
	(2.337)	(169.5)	(−652.485 08)	(−12)	
			[−652.527 90]	[−16.8]	
NaNCO (**13**)	2.259	168.7	−329.543 21	19.6	0.8
NaN_3 (**14**)	2.212	174.2	−325.672 63	4.3	9.3
	(2.455)	(172.7)	(−326.006 74)	(5.2)	
MgHNCS (**15**)	2.228	162.9	−690.495 61	24.24	8.1
AlH_2NCS (**18**)	2.106	157.6	−733.407 89	57.4	3.0
AlH_2N_3 (**20**)	1.978	165.8	−406.922 06	87.5	0.2

[a] Geometries are given at the MP2/6-31G**//MP2/6-31G** level of theory, with values in parentheses at the MP2/TZ2P//MP2/TZ2P level. The values in square brackets are at the MP4/TZ2P//MP2/TZ2P level. X–B represents the distance between the ligand atom and the central atom of the pseudohalide group; A–B–C is the angle of this functional group. [b] Structure number. Geometry obtained at the MP2/6-31G**//MP2/6-31G** level of theory. [c] Energy relative to the respective linear isomer, the isocyanate, the isothiocyanate, or the azide. [d] Barrier between the π-complex and the linear isomer from the side of the cyclic complex.

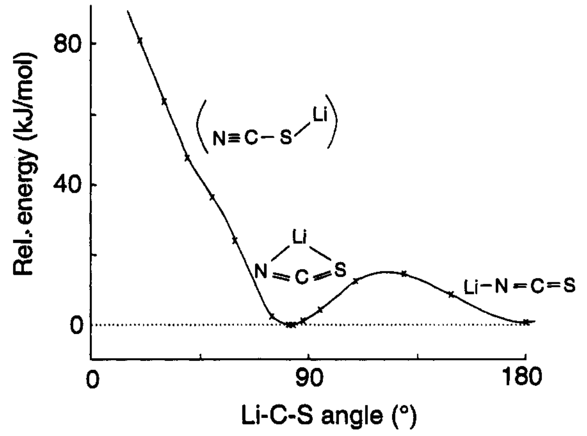

Figure 1. Potential energy diagram for the migration of the Li atom between the ends of the NCS group in LiNCS. Here the Li–C–S angle was varied, and the rest of the geometry was optimized at each point of the curve (at the 6-31G**/MP2 level). The inflection point at around 40° corresponds to the cyanate isomer, which is not a stable equilibrium structure.

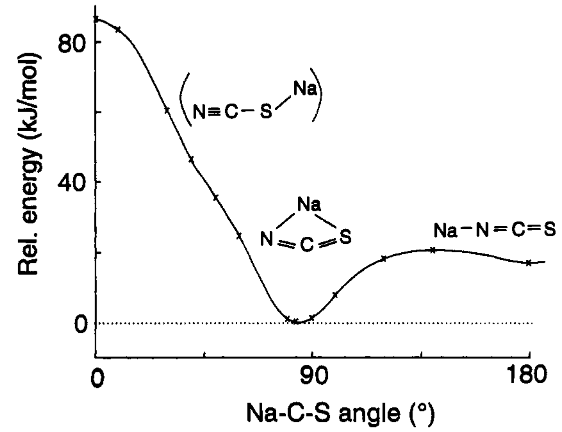

Figure 2. Potential energy diagram for the migration of the Na atom between the ends of the NCS group in NaNCS, with the geometry being relaxed at each point of the curve (at the 6-31G**/MP2 level).

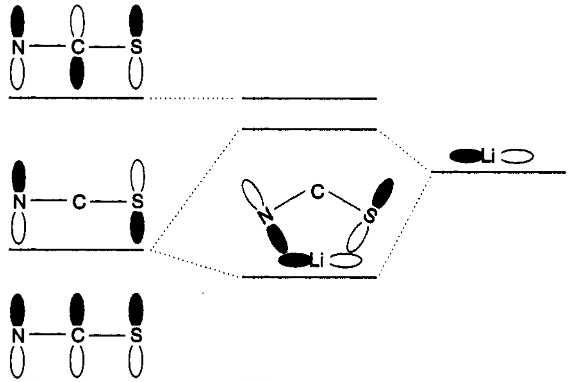

Figure 3. Bonding scheme in the cyclic complex using the example of LiNCS. All studied π-complexes bond in a similar way.

(cf. Figure 3). The bond within this functional group is weaker than that in other low-energy isomers, as signified by the respective bond lengths. On the other hand, the distance between the central atom of the functional group and the ligand is the shortest of the possible isomers in these complexes (see Table 1).

It is important to establish how the minima, found in this work for the cyclic complexes, depend on the level of theory used. In a previous ab initio work on LiNCO using small basis sets (STO-3G and 4-31G) at the Hartree–Fock (HF) level,[9,10] five possible structures were found. The isocyanate was thought to be the most stable, with the cyanate 33 kJ/mol higher in energy. The other three structures were in excess of 330 kJ/mol less stable. The π-complex in ref 9 was not found because of the small bases used and the lack of allowance for the correlation energy. In contrast, it was found in this work that even for LiNCS, where the energy minimum of the cyclic structure is more pronounced, the π-complex form lies 41.3 kJ/mol above the linear on using the same level of theory as in refs 9 and 10 (HF/4-31G). At the 6-31G**/MP2 level, the cyclic form is lower in energy (by 0.66 kJ/mol). Increasing the basis set further (TZ2P/MP2) seems to make the cyclic form slightly less stable (1 kJ/mol above the linear), while introducing more correlation at the TZ2P/MP4 level brings the energy of the cyclic form further down (5.19 kJ/mol below the linear, at the MP2 minimum). This indicates that the π-complexes are not artifacts of low-level calculations; their description requires the best possible description of the correlation energy. Furthermore, in view of a possible anionic dissociation path for these π-complexes, the effect of the augmentation of the basis with one extra diffuse (+) function was tested. This, however, had no significant effect on the equilibrium geometry.

From the point of later experimental identification of these compounds, there are two factors, that have to be taken into account: their thermodynamic stability with respect to the more stable isomers and the isomerization barrier. On both counts, the most promising two compounds are LiNCS (**5**) and especially NaNCS (**11**) (see Figures 1 and 2): their cyclic form is the global energy minimum, lying 0.7 and 17 kJ/mol, respectively, under the linear form. The isomerization barriers are also quite sizeable: 14.6 and 18 kJ/mol, respectively. It can be shown from the calculated harmonic force constants matrix that the potential energy surfaces, presented in Figures 1 and 2, correspond to a very good approximation to the torsional normal vibration of these molecules. The calculated harmonic torsional frequencies for cyclic LiNCS and NaNCS are 196 and 139 cm^{-1}, respectively, thus the zero-point torsional energies are 1.2 and 0.8 kJ/mol, respectively. These are negligible compared to the barrier heights, and this has two consequences: the cyclic forms of these molecules

Table 2. Calculated Equilibrium Harmonic Vibrational Frequencies (in cm^{-1}) and IR Intensities (in km/mol) for the Linear and Cyclic Isomers of LiNCS and NaNCS[a]

LiNCS-lin	2059 (1229)	964 (13)	599 (223)	484 (6)	91 (75)	
	ν_{asNCS}	ν_{sNCS}	ν_{LiN}	δ_{NCS}	δ_{LiNC}	
LiNCS-cyc	1984 (205)	779 (24)	634 (62)	421 (5)	417 (85)	196 (18)
	ν_{CN}	ν_{SC}	ν_{LiC}	δ_{NCS}	γ_{NCS}	δ_{ring}
NaNCS-lin	2055 (942)	883 (6)	331 (82)	474 (5)	52 (27)	
	ν_{asNCS}	ν_{sNCS}	ν_{NaN}	δ_{NCS}	δ_{NaNC}	
NaNCS-cyc	2005 (207)	762 (19)	517 (3)	286 (57)	421 (4)	139 (6)
	ν_{CN}	ν_{SC}	ν_{NaC}	δ_{NCS}	γ_{NCS}	δ_{ring}

[a] Infrared intensities are given in parentheses. Frequencies were calculated at the MP2/6-31G**//MP2/6-31G** level of theory. Frequencies are unscaled for reasons explained in the text. In order to achieve better agreement with experiments, the stretching frequencies (ν) must be multiplied by 0.9.[25]

will be stable in the vapor phase, and the use of a simple harmonic model with scaling gives an acceptable first estimate. Also, these potential wells have a much higher barrier along the stretching normal modes, and thus the calculated harmonic frequencies with scaling should also be reasonable for the stretches. In LiNCS, there are two equally deep minima, corresponding to the linear and the cyclic forms, and these are connected only via tunneling (the potential curves in Figures 1 and 2 are minimum energy pathways). Thus, in the LiNCS case, both forms will be stable and in equilibrium in the vapor phase. In NaNCS, the π-complex will be the major observable isomer.

The equilibrium vibrational frequencies of all compounds were calculated to make sure that the obtained structures are minimum energy forms. For the two most stable π-complexes, these frequencies can be used as diagnostic tools, particularly because the vibrational spectra of the linear and cyclic isomers are so different. Their equilibrium harmonic vibrational frequencies and intensities are given in Table 2. The best wavenumber regions to identify the LiNCS π-complex in a mixture of the two isomers from a low-resolution IR or Raman spectrum are the asymmetric and symmetric NCS stretch region and the region of the ring deformation frequency. However, the best method for their identification would be either microwave or high-resolution IR spectroscopy. It seems likely that sufficiently high concentrations can be obtained in the vapor phase, as both compounds have been shown to melt without decomposition at atmospheric pressure if water is carefully removed from the system.[20,21]

High-temperature photoelectron spectroscopy is another valuable method for the identification of molecules in the vapor phase[22,23] and it is also likely that these compounds will be easier to get in the vapor phase at low pressures. Although the vertical ionization energies, collected in Table 3, were obtained by using Koopmans' theorem, these will be useful for diagnostic purposes because the values are substantially different for the linear and cyclic forms.

Table 3. Vertical Ionization Energies (in eV) of the Lowest Energy Linear and Cyclic Isomers of LiNCS and NaNCS[a]

LiNCS	8.30π	13.21π	14.40σ	16.91σ
LiNCS-π	9.28, 9.70	13.96, 14.32	14.74	16.82
NaNCS	7.76π	12.61π	13.74σ	15.96σ
NaNCS-π	8.72, 9.00	13.29, 13.56	14.10	16.22

[a] Calculated using Koopmans's theorem at the MP2/TZ2P//MP2/TZ2P level.

It was shown above that the experimental identification of the cyclic form of LiNCS and NaNCS should be possible. The question arises as to whether other cyclic compounds could possibly be identified in the vapor phase. The experimental observation of the cyclic isomers with an energy of ~20 kJ/mol above the linear form (*kT* is ~4–10 kJ/mol at the melting point of these compounds) is probably not feasible. However, there is one more π-complex which has only a slightly higher energy than the linear form: NaN_3. It melts at atmospheric pressure without decomposition,[24] and thus it can be studied in the vapor phase. However, the small barrier size implies that the harmonic model for the vibrational frequencies is not meaningful. As the isomerization barrier is higher on the linear side (13.6 kJ/mol) than on the π-complex side (9.3 kJ/mol), the molecule is linear at the $v = 0$ state. As excited vibrational states, populated at the temperature of the molten salts, will be above the isomerization barrier, the molecule will carry out a large-amplitude, hindered torsional motion, and its vibrational and rotational spectra in the excited vibrational states will be very different from what would be expected if only the linear form existed.

Conclusions

Ab initio calculations on different pseudohalides revealed the existence of a new isomer: a four-membered planar ring. The bonding in the new π-complex isomer is achieved between the empty p-orbital of the ligand atom and the π-system of the pseudohalide functional group. A good description of the bonding in these molecules requires the inclusion of the correlation energy. These π-complexes were shown to be stable equilibrium structures for different pseudohalides with -NCO, -NCS, and -N_3 substituents. In two cases, LiNCS and NaNCS, the π-complex is the most stable isomer. Thus it seems likely that if these molecules can be brought into the vapor phase at sufficiently high concentrations and without decomposition, the existence of the π-complexes can also be shown experimentally.

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