The $(Me_2N)_2CO{\cdot}SiCl_4$ complex: the first case of ligand equatorial orientation in a trigonal bipyramide

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The structure of the tetrachlorosilane–tetramethylurea complex suggested from NQR data is proved by X-ray crystallography; experimental data is compared with calculated values.

Previously,[1] studying the complex formation of tetrachlorides of Group 14 elements by ^{35}Cl NQR spectroscopy, we have shown that in the trigonal bipyramidal complex $(Me_2N)_2CO{\cdot}SiCl_4$ **1** the ligands occupy an equatorial position which is quite unexpected for complexes of this type. It is only recently that a $SiCl_4$ complex with an imidazole carbene derivative having the same equatorial ligand orientation has been reported.[2]

Continuing our studies, we carried out AM1, MNDO and PM3 quantum-chemical calculations with full optimization of geometry of the various structures of this complex (with axial and equatorial ligand disposition) and the initial components. We have also performed an X-ray study of this complex.† The results are presented in Tables 1–3.

As can be seen from Table 1, all calculations give stable structures **1** with equatorial and axial ligand orientations. However, AM1 provides a more stable axial position and positive enthalpy of complex formation. MNDO and PM3 calculations are in better agreement with experimental values and give a lower enthalpy of formation with a negative enthalpy of reaction value with equatorial orientation. The low reaction enthalpies are consistent with the fact that the formation of this complex is a reversible process. On heating the complex over 85% of the initial components was isolated, which is quite unexpected taking into account the fact that the coordinated O–Si bond length is nearly equal to that of the covalent bond. The experimental enthalpies of similar reactions are close to the calculated values.[3]

PM3 proved to be the best method for comparison of geometry parameters (Tables 2 and 3) since it results in the least deviations from the experimental values.

Satisfactory correlations between the calculated and experimental energy and geometry parameters of compound **1** enable the donor–acceptor charge transfer to be evaluated (*ca.* 0.3–0.4 electrons depending on the calculation method) (Table 1).

As follows from the X-ray data, the main features of molecule **1** (Figure 1) are the presence of a hypervalent fragment and slightly abnormal electron density distribution. The Si atom coordination polyhedron (trigonal bipyramidal), is nearly symmetrical with respect to the equatorial plane (the Si atom is only 0.01 A displaced from the plane) and it is this form (axial Cl atoms and equatorial O and Cl) that has never been seen in the known structures of pentacoordinated organosilicon derivatives. The equatorial Si–O and Si–Cl bonds (Table 2) are 0.05–0.07 A longer than normal bonds in structures having pentacoordinated Si atoms.[4,5] It is likely that lengthening of this kind is typical of the pentacoordinated silicon atom with a strongly electronegative environment: in

Table 1 Enthalpies of formation (H) and enthalpies of reactions (ΔH) of equatorial (Eq) and axial (Ax) complex **1** structures, calculated by semiempirical methods, and charge transfer values (Δq).

Method of calculations	$\Sigma H_{init.}$	Eq			Ax		
		H_{Eq}	ΔH_{Eq}	Δq	H_{Ax}	ΔH_{Ax}	Δq
AM1	−194.73	−187.06	7.67	0.2879	−197.48	−2.75	0.0378
MNDO	−177.90	−183.70	−5.80	0.2906	−182.65	−4.75	0.2311
PM3	−203.47	−212.76	−9.29	0.3915	−210.82	−7.35	0.2518

† *Crystal data for* **1**. Triclinic crystals, $a = 6.641(2)$, $b = 7.344(3)$, $c = 12.788(4)$ A, $\alpha = 75.33(2)$, $\beta = 81.97(2)$, $\gamma = 82.97(2)^\circ$, $V = 595.0(5)$ A^3, $D_x = 1.597$ g cm^{-3}, $Z = 2(C_5H_{12}N_2OSiCl_4)$, $P1$ space group. The structure was solved by direct method and refined by the full-matrix least-squares procedure in an anisotropic approximation for non-hydrogen atoms and isotropic for H atoms localized in the difference synthesis. Corrections for absorption ($\mu = 10.7$ cm^{-1}) were introduced by DIFABS program.[8] The final divergence factor values are $R = 0.042$, $R_w = 0.044$ basing on 1317 reflections with $I > 3\sigma(I)$. Coordinates and heat parameters are presented in Table 2. All the calculations were made on an IBM PC/AT computer using MOPAC 6.0 and SHELXTL PLUS programs.[9] X-ray diffraction experiment was performed at 180 K on a Syntex $P2_1$ diffractometer, Mo-Kα, graphite monochromator, $\theta/2\theta$ scan, $2\theta_{max} = 46^\circ$. Full lists of bond lengths, bond angles, atomic coordinates and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre (CCDC). For details, see 'Notice to Authors', *Mendeleev Communications*, 1996, Issue 1. Any request to the CCDC for data should quote the full literature citation and the reference number 1135/10.

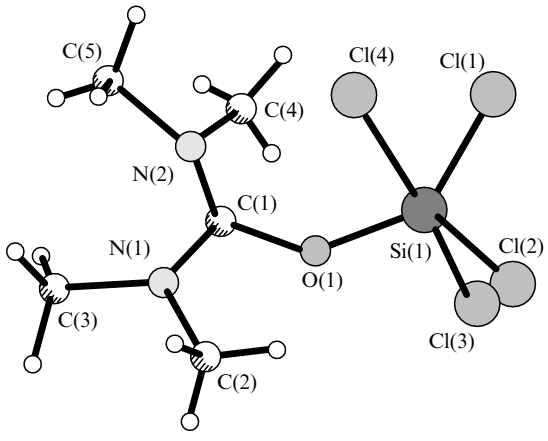

Figure 1 The structure of crystalline **1**.

Table 2 Compound **1** bond lengths.

Bond	Bond length/A			
	Exp.	AM1	MNDO	PM3
Cl(1)–Si(1)	2.073(3)	2.082	2.129	2.075
Cl(2)–Si(1)	2.082(3)	2.075	2.130	2.073
Cl(3)–Si(1)	2.176(3)	2.155	2.209	2.161
Cl(4)–Si(1)	2.209(3)	2.278	2.205	2.392
Si(1)–O(1)	1.696(3)	1.904	1.745	1.729
O(1)–C(1)	1.338(5)	1.319	1.269	1.313
N(1)–C(1)	1.322(5)	1.373	1.426	1.379
N(1)–C(2)	1.468(6)	1.447	1.481	1.487
N(1)–C(3)	1.481(6)	1.439	1.481	1.479
N(2)–C(1)	1.311(5)	1.396	1.370	1.425
N(2)–C(4)	1.463(5)	1.446	1.485	1.487
N(2)–C(5)	1.471(7)	1.443	1.489	1.487

the structures of four lactam derivatives possessing similar Si atoms[6] with four O or Cl atoms present, the average length of the equatorial Si–Cl bonds is 2.0056 A, whereas the equatorial Si–O(Me) bond in one of the structures is only 1.680(2) A. A greater bond length in molecule **1** may be caused by further increasing the negativity of the Si atom environment. An analogous lengthening of the equatorial Si–F bonds in diorganyltrifluorosilicate anions[7] with halogen atoms in the equatorial position should also be noted.

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Table 3 Valent angles (ω) of **1**.

Angle ω	Angle ω/°			
	Exp.	AM1	MNDO	PM3
Cl(1)–Si(1)–Cl(2)	116.6(1)	120.8	125.0	121.5
Cl(1)–Si(1)–Cl(3)	90.9(1)	95.2	92.1	97.0
Cl(2)–Si(1)–Cl(3)	92.5(1)	95.6	92.0	98.0
Cl(1)–Si(1)–Cl(4)	90.5(1)	91.1	91.9	88.1
Cl(2)–Si(1)–Cl(4)	90.9(1)	91.5	91.8	88.2
Cl(3)–Si(1)–Cl(4)	175.3(1)	166.3	171.5	168.3
Cl(1)–Si(1)–O(1)	126.0(1)	119.6	117.5	120.1
Cl(2)–Si(1)–O(1)	117.4(1)	119.3	117.5	116.6
Cl(3)–Si(1)–O(1)	85.9(1)	83.5	85.8	87.7
Cl(4)–Si(1)–O(1)	89.7(1)	82.8	85.7	80.1
Si(1)–O(1)–C(1)	132.7(3)	129.8	171.9	127.2
C(1)–N(1)–C(2)	121.8(3)	119.1	121.0	119.4
C(1)–N(1)–C(3)	121.9(3)	122.6	121.5	123.7
C(2)–N(1)–C(3)	116.3(3)	118.2	117.5	114.8
C(1)–N(2)–C(4)	121.3(3)	118.0	117.2	116.4
C(1)–N(2)–C(5)	121.8(3)	119.9	116.7	117.9
C(4)–N(2)–C(5)	115.3(3)	116.4	116.8	113.1
O(1)–C(1)–N(1)	116.2(3)	116.8	119.9	115.3
O(1)–C(1)–N(2)	119.3(3)	118.5	120.6	118.2
N(1)–C(1)–N(2)	124.4(3)	124.0	119.4	124.3

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