Geometry and Stabilization of the $Ni_2Cl_8^{4-}$ Anion in $[HN(C_2H_4)_3NCH_3NiCl_4]_2$[1]

F. K. Ross and G. D. Stucky

Contribution from the Department of Chemistry and Chemical Engineering and Materials Research Laboratory, University of Illinois, Urbana, Illinois 61801.

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Abstract: A three-dimensional X-ray diffractometer study of the compound bis-*N*-methyl-*N′*-diazabicyclo[2.2.2]-octonium di-μ-chloro-hexachlorodinickelate(II), $[HN^+(C_2H_4)_3N^+CH_3NiCl_4]_2$, has been performed. Refinement using full-matrix least-squares methods on 1342 observed reflections led to a final *R* value of 5.9% (based on *F*). The molecule crystallizes in the orthorhombic space group Pbca with unit cell dimensions $a = 13.708$, $b = 13.482$, $c = 13.555$ Å, $\rho_{obsd} = 1.73$ g/cc, $\rho_{calcd} = 1.74$ g/cc for four dimeric formula units. The complex was found to contain the unusual $Ni_2Cl_8^{2-}$ anion with five-coordinate Ni^{2+} ions in an approximately square-pyramidal geometry. The two square pyramids which make up the anion have one common basal edge; a crystallographic inversion center is located at the midpoint of this edge so that the apices project in opposite directions. The bridging chlorine atoms are not symmetrically disposed between the nickel atoms (distances are 2.366 *vs.* 2.499 Å). Stabilization results from the formation of a bifurcated hydrogen bond between the proton of the cation and the two nonbridging basal chlorine atoms of the anion.

The structure and properties of the various compounds formed by Ni(II) with halide ligands have been of continuing interest to us and have been extensively investigated in our laboratories. The majority of these compounds fall into two simple classes; those of structural formula $RNiX_3$ containing six-coordinate Ni(II) in chains of face-shared octahedra, and those of formula R_2NiX_4, which contain NiX_4^{2-} tetrahedra. The stabilization of these structures is found to be a direct function of cation size, with larger cations requiring the less restrictive lattice of the NiX_4^{2-} structure. Thus, $KNiCl_3$[2a] and $RbNiCl_3$[2b] are representative of the first structural type, larger cations such as $[(C_6H_5)_3AsCH_3]^+$ and $[(C_2H_5)_4N]^+$ give only tetrahedral geometries,[3,4] and cations of intermediate size can lead to either geometry (cesium[5,6] or tetramethylammonium[7–10] ions, for example).

Five-coordinate compounds of Ni(II) with halide ligands have not been reported, although such compounds are known for Cu(II)[11] and for Mn(II)[12] in the form of MCl_5^{3-} ions. These compounds and the similar $Ni(CN)_5^{3-}$ ion[13] are stabilized by large trivalent cations which are also capable of hydrogen bonding. Spectroscopic and magnetic data indicated that $[CH_3^+\text{-}N(CH_2CH_2)_3N^+H]NiCl_4$ contains five-coordinate nickel atoms[14] with only chloride ions as ligands. A single-crystal X-ray study was undertaken to verify this proposed structure and to investigate the effects of hydrogen bonding and steric interactions on the coordination sphere of the nickel atom.

Experimental Section

Crystals of the title compound were prepared by Dr. V. L. Goedken[14] and were well-formed parallelepipeds or polyhedra. Larger crystals appeared red-violet in transmitted light while microcrystals were observed to be bright red. The compound is moderately hygroscopic; the crystals selected for examination were protected by a thin coating of oven-dried silicone grease and were sealed in 0.5-mm thin glass capillaries. A thin parallelepiped with well-formed faces was used for preliminary investigation. Precession photography indicated that this crystal was of orthorhombic symmetry. The systematic absences of *h0l* for $l \neq 2n$, *0kl* for $k \neq 2n$, and *hk0* for $h \neq 2n$ are consistent only with the centric space group Pbca.

For data collection, a more uniform fragment of a crystal was selected. It was approximately ellipsoidal with axes 0.28 × 0.35 × 0.40 mm and was mounted in a soft glass capillary with its longest dimension parallel to the rotation axis. The crystallographic axes were located and identified by comparison with the axes assigned in the crystal studied previously. The rotation axis was found to be the [213] direction. This crystal was mounted on a Picker four-circle diffractometer for subsequent investigation; the sin θ/λ values of 18 carefully centered high-angle reflections were used to obtain lattice parameters[15] of $a = 13.708\,(6)$,[16] $b = 13.482\,(6)$, $c = 13.555\,(6)$ Å, $\alpha = \beta = \gamma = 90°$ ($T = 23°$, λ (CuKα_1) 1.54051 Å). The density calculated for eight monomeric units ($C_7H_{16}N_2NiCl_4$) per cell is 1.73 g/cm^3 and agrees well with the value of 1.74 (2) g/cm^3 measured by the flotation method in a mixture of *p*-bromotoluene and iodobenzene. Thus, no crystallographic symmetry is imposed for monomers containing $NiCl_4^{2-}$ ions. Dimeric anions, however, are required to contain a crystallographic center of inversion.

As this crystal was not mounted about a major crystallographic direction, the effects of multiple diffraction were assumed to be negligible during data collection. Molybdenum radiation was used to minimize errors in the absorption correction (μ (MoKα) =

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Table I. Observed and Calculated Structure Factors in Electrons for $[C_7H_{16}N_2]_2Ni_2Cl_8$. Unobserved Reflections Are Indicated with an Asterisk.

[illegible]

23.73, μ (CuKα) = 98.13 cm^{-1}). The incident and diffracted beams were passed through 1.5- and 2.0-mm pinhole collimators respectively, and a 0.005-in. zirconium foil filter was placed at the detector (a scintillation counter mounted 21 cm from the crystals). The takeoff angle was 1.0° and the lower level of the pulse height analyzer was adjusted to pass 90% of the Kα peak. ω scans of several intense reflections indicated a satisfactorily low mosaic character.

Peak scans were made at a rate of 1.0°/min using the θ-2θ technique. Scans of 1.00 and 1.33° were made, respectively, for peaks below and above 25° in 2θ. The scans were centered symmetrically about the position calculated for Kα (average) with stationary

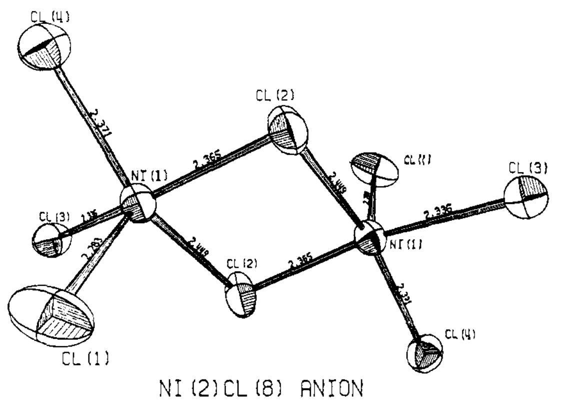

Figure 1. Molecular plot with thermal ellipsoids for the $Ni_2Cl_8^{4-}$ anion in $[C_7H_{16}N_2]_2Ni_2Cl_8$.

crystal–stationary counter background measurements of 40 sec each taken at either end of the scan. The stabilities of the crystal and of the instrumentation were monitored by periodically measuring several reflections. One octant of data (1988 reflections exclusive of space group absences) was collected within a maximum 2θ of 50°. Of these reflections, 646 were judged to be unobserved. The criterion used for assigning unobserved reflections was $I_{obsd} < 3\sigma(I)$ where $\sigma(I)$ is given by

$$\sigma(I) = [\sigma^2(\text{peak}) + \sigma^2(\text{background})]^{1/2}$$

Values for σ(peak) and σ(background) are the statistical errors associated with the integrated peak counts and with the background counts, respectively. Reflections were reduced to structure factors by correcting for absorption, Lorentz, and polarization effects.[17]

Solution and Refinement of the Structure. A three-dimensional Patterson map was calculated[18] and the largest peaks on the Harker lines (u, $^1/_2$ 0), (0, v, $^1/_2$), and ($^1/_2$, 0, w) provided the coordinates of the nickel atom. Similar sets of peaks were attributed to the four nonequivalent sets of chlorine atoms, but no coordinates could be determined with sufficient confidence to include any chlorine atoms in the first structure factor calculation. This calculation, phased on the nickel atom alone, provided a value of R_1 $(= \Sigma(|F_o| - |F_c|)/\Sigma|F_o| \times 100)$ of 62.2%. All chlorine atoms were located in a Fourier electron-density map produced from this set of structure factors. Inclusion of these atoms followed by several cycles of least-squares[19] refinement reduced R_1 to 44%. A second electron-density map revealed the coordinates of all remaining nonhydrogen atoms. Two cycles of least-squares refinement varying positional parameters for all atoms followed by three cycles with varying isotropic thermal parameters reduced R_1 to 15%. A difference Fourier map did not indicate strongly anisotropic thermal motion for any atoms nor did it clearly reveal hydrogen atom coordinates. Two further cycles of refinement with all thermal parameters varied anisotropically led to a value of R_1 = 10.7%. A second difference Fourier map was calculated and all hydrogen atom coordinates except those of the hydrogen atom bonded to the nitrogen atom could be estimated from it. The observed coordinates were in reasonable agreement with theoretical coordinates calculated for a tetrahedral geometry about carbon atoms. Inclusion of the hydrogen atoms at their calculated coordinates and one additional cycle of least-squares refinement reduced R_1 to 10.0%. The corresponding value of R_2 $(= [\Sigma w(|F_o| - |F_c|)^2/\Sigma w|F_o|^2]^{1/2} \times 100)$ was 10.2%.

At this time a plot of $(\Delta F)^2$ *vs.* F_o indicated that a significant reduction in the weights applied to reflections of moderate to high intensity was appropriate (unit weights had been used). A weighting scheme based on $\omega = 1/\sigma^2(F)$, where[20]

$$\sigma(F) = \frac{|F|}{2I}[\sigma^2(\text{peak}) + \sigma^2(\text{background}) + K^2I^2]^{1/2}$$

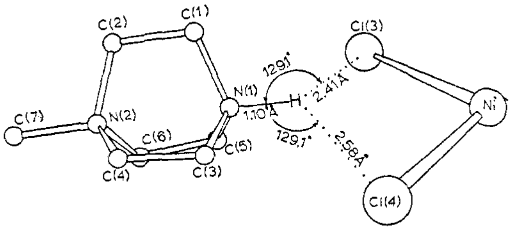

Figure 2. Hydrogen bonding in $[C_7H_{16}N_2]_2Ni_2Cl_8$.

was applied and the unobserved reflections were introduced into the data set. The value of K was 0.03. Three cycles of refinement varying all parameters (isotropic thermal parameters for hydrogen atoms) reduced R_2 to 6.9% for all reflections. The corresponding values of R_1 (observed data only) and ERF $(= [\Sigma w(|F_o| - |F_c|)^2/(N_o - N_v)]^{1/2}$, where N_o is the number of observations and N_v is the number of parameters varied) were 5.9% and 1.50, respectively.

The resulting calculated structure factors along with the observed values are given in Table I. Atomic form factors for Ni^0, Cl^0, O^0, N^0, C^0, and H^0 were taken from "International Tables for X-ray Crystallography," 1962, Table 3.3.1A; anomalous dispersion corrections (f' and f'') for nickel and chlorine were taken from Cromer[21] and were applied to the calculated structure factors. Standard deviations in bond distances and angles were calculated[22] from the final cycle of refinement and computer-drawn plots of the molecular and crystal structures were generated by Johnson's plotting program.[23] A final difference Fourier was calculated and was found to be free of peaks larger than one-half the magnitude of those chosen as hydrogen atom peaks (~0.5 electron/Å^3).

Discussion of the Structure

The compound was found to contain five-coordinate Ni(II) in the form of a bridged binuclear anion, $Ni_2Cl_8^{4-}$. The structure of this anion, shown in Figure 1, is unique in nickel chemistry as reported at present. It is best described as two square pyramids sharing a common edge. A crystallographic inversion center is located midway between the nickel atoms; this requires both pyramids to be identical but with apices (Cl(1)) pointing in opposite directions. A notably similar structure is reported for $(ClN)_2V_2Cl_6$[24] in which the –NCl group occupies the apical position. The ellipsoids plotted in Figure 1 indicate the relative thermal motion of the atoms; the actual root mean square components of thermal vibration along the axes of these ellipsoids are given in Table II. Thermal motion is observed to be nearly isotropic for all atoms of the anion except Cl(1) and Cl(2). The motion of Cl(2) is, as expected, chiefly perpendicular to the bridge bonds. Anisotropy of thermal vibration for Cl(1) apparently results from steric interactions. The packing of cations and anions in the unit cell is shown in the stereoscopic pair of drawings labeled Figure 3. The only atoms of adjacent molecules found within 3.5 Å of Cl(1) are hydrogen atoms of nearby ethylene chains of the cation. The predominant motion of Cl(1) is approximately parallel

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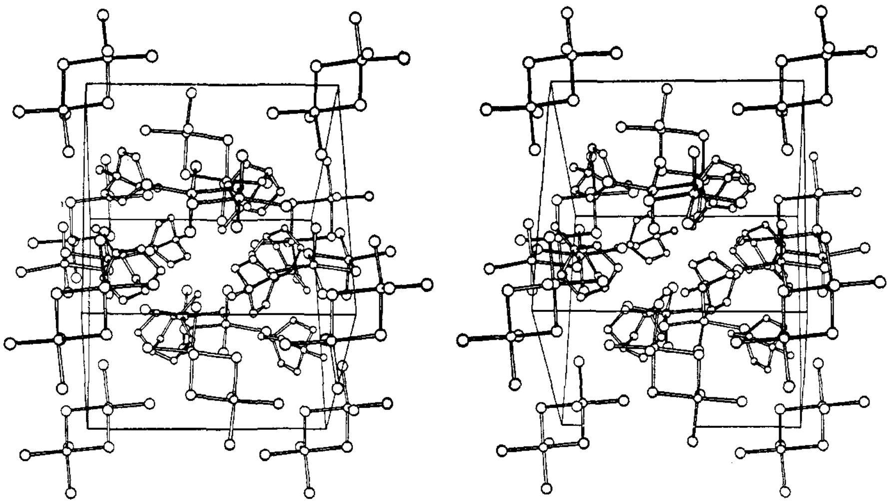

Figure 3. Stereoview of the contents of the unit cell for $[C_7H_{16}N_2]_2Ni_2Cl_8$.

Table II. Root Mean Square Components of Thermal Vibration for $[C_7H_{16}N_2]_2Ni_2Cl_8$

Atom	$R(1)$, Å	$R(2)$, Å	$R(3)$, Å
Ni	0.1607	0.1755	0.1894
Cl(1)	0.1810	0.2003	0.3085
Cl(2)	0.1636	0.1706	0.3031
Cl(3)	0.1685	0.1847	0.2163
Cl(4)	0.1795	0.1920	0.2282
N(1)	0.1818	0.2033	0.2145
N(2)	0.1626	0.1835	0.2020
C(1)	0.1775	0.2060	0.2757
C(2)	0.1624	0.2046	0.2336
C(3)	0.1856	0.2160	0.2451
C(4)	0.1600	0.1977	0.2275
C(5)	0.1581	0.1886	0.2453
C(6)	0.1566	0.1956	0.2035
C(7)	0.1666	0.2252	0.2614

to these chains, presumably to minimize interactions with hydrogen atoms.

The smaller vibrational amplitudes of Cl(3) and Cl(4) and their closer proximity to N(1) suggest that their motion is reduced by hydrogen bonding. In fact, a hydrogen atom placed along a line of minimum interaction with the other three bonds to N(1) projects between Cl(3) and Cl(4), as shown in Figure 2. The resulting bifurcated hydrogen bond has H···Cl distances which are 0.58 and 0.42 Å less than the sum of the van der Waals radii, and N^+–H···Cl distances (3.22 and 3.36 Å) which are similar to those found in NH_4Cl and in amine hydrochlorides.[25] The N–H bond length was arbitrarily chosen to be 1.10 Å. Although the true position of the hydrogen atom which is bonded to N(1) could not be determined in this experiment, no reasonable position could be found where the effects of hydrogen bonding could be considered negligible. A similar interaction lengthens two Ni–Cl bonds in the five-coordinate compound $CH_3N(CH_2)_3NNiCl_3 \cdot H_2O$[26] in which the resulting Ni–Cl distances are 2.281 (2) and 2.339 (2) Å, respectively, for no hydrogen bond interaction and for hydrogen-bonded chloride ligands. These distances are in agreement with the values found in the $Ni_2Cl_8^{4-}$ anion; specifically, 2.283 (2) Å for the nonhydrogen-bonded Cl(1) and 2.336 (2) and 2.371 (2) Å for Cl(3) and Cl(4). The importance of this hydrogen-bonding interaction in stabilizing this crystal structure is also emphasized by the observation[14] that the complex cannot be formed with bromo or iodo ligands or with the dimethylated cation.

Table III. Best Least-Squares Planes for the $[C_7H_{16}N_2]_2Ni_2Cl_8$ Square Pyramid

Distances (Å) of atoms from plane						
Atom	Ni	Cl(1)	Cl(2)	Cl(3)	Cl(4)	Cl(2)′
Distance	−0.502 (2)	−2.777 (2)	0.024 (2)	0.022 (2)	−0.022 (2)	−0.025 (2)

Plane determined by Cl(2), Cl(3), Cl(4)

Equation of plane[a] $0.5430x + 0.0027y - 0.8452z + 0.0001 = 0$

[a] Equation given is $AX + BY + CZ + D = 0$ where X, Y, and Z are scaled orthogonal coordinates related to the fractional coordinates in the orthorhombic cell by $X = ax$, $Y = by$, $Z = cz$.

A least-squares fitting procedure was used to determine the coplanarity of the chlorine atoms Cl(2), Cl(3), Cl(4), and Cl(2)′. The results of this calculation (Table III) show that all four chlorine atoms are less than 0.025 Å from the plane and that the nickel atom lies 0.5 Å above it. As can be seen for the anion in Figure 1, the primary deviation from C_{4v} symmetry about the nickel atom results from the positioning of one bridging chlorine atom. The separation of nickel atoms (3.669 Å) is considerably greater than the sum of their covalent radii (2.48 Å for Ni^0), precluding any possibility of Ni–Ni bonding.

Table IV compares uncorrected Ni–Cl bond distances with those corrected for thermal motion (riding model),

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Table IV. Comparisons for Corrected and Uncorrected Bond Lengths for $[C_7H_{16}N_2]_2Ni_2Cl_8$

Bond	Uncorrected	Corrected riding model
Ni–Cl(1)	2.283	2.299 (2)
Ni–Cl(2)	2.366	2.378 (2)
Ni–Cl(3)	2.336	2.340 (2)
Ni–Cl(4)	2.371	2.377 (2)
Ni–Cl(2)′	2.449	2.460 (2)

and only slight increases are observed. Values of final positional and thermal parameters for all atoms, selected interatomic distances, and angles are given in Tables V, VI, and VII, respectively. Dihedral angles for the N–C–C–N chains of the cation (Table VIII) indicate a lack of planarity in each. These angles are consistent with a twisting of approximately 14° about the threefold axis of the cation (see Figures 2 and 3). A similar effect has been observed in several other structures involving the 1,4-diazabicyclo[2.2.2]octane system,[27,28] and possibly results from strain imposed by larger than tetrahedral angles about N(1).

Two notable features of the structure are the asymmetric nickel–chlorine–nickel bridge distances (2.449 and 2.336 Å) and the exceptionally close approach of the bridging chlorine atoms (3.119 Å). If the assumption is made that intraring chlorine–chlorine repulsions are primarily responsible for halogen-bridged four-membered ring geometries, a plot of the metal–bridge distances *vs.* the secant of one-half the bridge angles can be expected to yield a straight line according to the equation MB = BB/2 sec (α/2), where MB is the metal–bridge chlorine distance, BB is the bridge chlorine–bridge chlorine distance, and α is the metal–bridge chlorine–metal angle. The results of such an analysis for 17 chlorine-bridged four-membered ring systems reported in the literature are given in Table IX and Figure 4. Systems with four-, five-, and six-coordinate metals are included. In Figure 4, the systems are divided in two groups, those with all metal–chlorine bridged distances equal and those with opposite metal–chlorine bridged distances equal but adjacent metal–chlorine distances unequal. The latter are referred to as asymmetric bridge systems in this paper. Excluding $[GaCl_3]_2$ (Cl–Cl = 3.35 Å), the average bridge chlorine–bridge chlorine distance is

Table V. Positional and Thermal Parameters[a] for $[C_7H_{16}N_2]_2Ni_2Cl_8$

Atom	X	Y	Z	β_{11}[b]	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}	B[c]
Ni	0.0605 (1)	0.0866 (1)	0.0845 (1)	34 (1)	36 (1)	30 (1)	2 (1)	−3 (1)	2 (1)	
Cl(1)	−0.0206 (1)	0.0867 (1)	0.2317 (1)	66 (1)	69 (1)	44 (1)	26 (1)	17 (1)	13 (1)	
Cl(2)	0.0618 (1)	0.0890 (1)	−0.0386 (1)	64 (1)	36 (1)	57 (1)	13 (1)	−33 (1)	−12 (1)	
Cl(3)	0.2204 (1)	0.0664 (1)	0.1406 (1)	32 (1)	39 (1)	46 (1)	−1 (1)	−5 (1)	5 (1)	
Cl(4)	0.0864 (1)	0.2593 (1)	0.0643 (1)	39 (1)	35 (1)	56 (1)	−1 (1)	−2 (1)	1 (1)	
N(1)	0.2211 (4)	0.2656 (4)	0.2713 (4)	47 (3)	42 (3)	40 (3)	−1 (2)	2 (2)	−5 (2)	
N(2)	0.3248 (4)	0.3779 (4)	0.3732 (3)	38 (3)	36 (3)	34 (3)	5 (2)	5 (2)	−1 (2)	
C(1)	0.2574 (6)	0.2087 (5)	0.3578 (5)	77 (5)	36 (4)	47 (4)	−3 (3)	9 (4)	3 (3)	
C(2)	0.3086 (5)	0.2840 (4)	0.4287 (5)	55 (4)	32 (3)	44 (4)	4 (4)	3 (3)	7 (3)	
C(3)	0.1612 (5)	0.3521 (6)	0.3036 (5)	41 (4)	62 (5)	48 (4)	9 (4)	4 (3)	−2 (4)	
C(4)	0.2278 (5)	0.4254 (5)	0.3536 (5)	47 (4)	35 (4)	42 (4)	12 (3)	1 (3)	1 (3)	
C(5)	0.3050 (5)	0.3007 (5)	0.2094 (5)	50 (4)	38 (4)	42 (4)	10 (3)	18 (3)	−1 (3)	
C(6)	0.3751 (5)	0.3569 (5)	0.2767 (4)	39 (4)	42 (4)	31 (4)	0 (3)	8 (3)	−1 (3)	
C(7)	0.3880 (6)	0.4484 (5)	0.4336 (6)	56 (5)	44 (4)	58 (5)	−17 (4)	3 (4)	−10 (4)	
H(1A)[e]	0.303 (6)	0.161 (5)	0.335 (5)							5.00[d]
H(1B)	0.200 (6)	0.155 (6)	0.384 (5)							2.12
H(2A)	0.366 (6)	0.266 (6)	0.449 (5)							2.73
H(2B)	0.271 (6)	0.300 (6)	0.486 (6)							1.59
H(3A)	0.124 (7)	0.321 (6)	0.353 (6)							0.94
H(3B)	0.129 (6)	0.372 (7)	0.247 (7)							1.49
H(4A)	0.211 (8)	0.453 (8)	0.408 (7)							5.00
H(4B)	0.250 (9)	0.471 (11)	0.318 (8)							7.71
H(5A)	0.268 (6)	0.341 (7)	0.179 (6)							3.33
H(5B)	0.337 (8)	0.246 (7)	0.183 (6)							5.00
H(6A)	0.382 (8)	0.417 (7)	0.259 (7)							5.00
H(6B)	0.432 (7)	0.312 (7)	0.294 (7)							1.54
H(7A)	0.399 (8)	0.511 (8)	0.395 (7)							5.00
H(7B)	0.363 (6)	0.454 (5)	0.497 (6)							2.11
H(7C)	0.454 (8)	0.422 (7)	0.455 (6)							1.41

[a] Values listed × 10^4. [b] The form of the anisotropic thermal ellipsoid is given by $\exp[-(\beta_{11}h^2 + \beta_{22}k^2 + \beta_{33}l^2 + \beta_{12}hk + \beta_{13}hl + \beta_{23}kl)]$. [c] Isotropic temperature factors of the form $\exp -B(\sin^2 \theta)/2$ were used for hydrogen atoms. [d] Hydrogen temperature factors which could not be refined were set equal to 5.00. [e] The numbers in parentheses refer to the carbon atom to which the hydrogen atom is bonded.

Table VI. Selected Interatomic Distances for $[C_7H_{16}N_2]_2Ni_2Cl_8$

Atoms	Distance, Å	Atoms	Distance, Å
Bonded		C(1)–C(2)	1.566 (9)
Ni–Cl(1)	2.283 (2)	C(3)–C(4)	1.504 (9)
Ni–Cl(2)	2.366 (2)	C(5)–C(6)	1.525 (9)
Ni–Cl(2)′	2.449 (2)		
Ni–Cl(3)	2.336 (2)	Nonbonded	
Ni–Cl(4)	2.371 (2)	Ni–Ni′[a]	3.669 (2)
N(1)–C(1)	1.492 (8)	Cl(2)–Cl(2)′	3.119 (2)
N(1)–C(3)	1.496 (8)	N(1)–Cl(3)	3.218 (5)
N(1)–C(5)	1.497 (8)	N(1)–Cl(4)	3.361 (5)
N(2)–C(2)	1.486 (7)	Cl(2)′–C(5)	3.304 (6)
N(2)–C(4)	1.497 (8)	Cl(2)′–C(6)	3.420 (6)
N(2)–C(6)	1.512 (7)	Cl(1)′–C(3)	3.734 (7)
N(2)–C(7)	1.529 (8)	Cl(1)′–C(4)	3.760 (6)

[a] Atoms marked with a prime are related to unprimed atoms by a symmetry operation.

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Table VII. Selected Angles for $[C_7H_{16}N_2]_2Ni_2Cl_8$

Atoms	Angle, deg	Atoms	Angle, deg
Cl(1)–Ni–Cl(2)	105.75 (8)	C(1)–N(1)–C(3)	110.6 (5)
Cl(1)–Ni–Cl(3)	99.95 (7)	C(1)–N(1)–C(5)	110.7 (5)
Cl(1)–Ni–Cl(4)	100.02 (7)	C(3)–N(1)–C(5)	109.9 (5)
Cl(2)–Ni–Cl(3)	153.61 (7)	N(2)–C(2)–C(1)	108.4 (5)
Cl(2)–Ni–Cl(4)	90.65 (6)	N(2)–C(4)–C(3)	109.8 (5)
Cl(3)–Ni–Cl(4)	90.68 (6)	N(2)–C(6)–C(5)	108.5 (5)
Cl(2)–Ni–Cl(2)′ [a]	80.71 (6)	C(2)–N(2)–C(4)	108.7 (5)
Ni–Cl(2)–Ni′	99.29 (6)	C(2)–N(2)–C(6)	110.1 (5)
N(2)–N(1)–Cl(3)	144.5 (3)	C(4)–N(2)–C(6)	109.6 (4)
N(2)–N(1)–Cl(4)	142.4 (3)	C(2)–N(2)–C(7)	109.9 (5)
N(1)–C(1)–Cl(2)	106.9 (5)	C(4)–N(2)–C(7)	109.8 (5)
N(1)–C(3)–C(4)	108.0 (5)	C(6)–N(2)–C(7)	108.8 (5)
N(1)–C(5)–C(6)	108.0 (5)	N(1)–N(2)–C(7)	178.9 (4)

[a] Primed atoms are related to unprimed atom by a center of inversion at the origin.

Table VIII. Dihedral Angles for $[C_7H_{16}N_2]_2Ni_2Cl_8$

Atoms defining plane 1	Atoms defining plane 2	Angle, deg
Cl(2)–Ni–Cl(2)′ [a]	Cl(1)–Ni–Cl(3)	102.66 (7)
Cl(2)–Ni–Cl(2)′	Cl(1)–Ni–Cl(4)	75.29 (8)
Cl(2)–Ni–Cl(2)′	Cl(3)–Ni–Cl(4)	33.43 (6)
Cl(2)–Ni–Cl(1)	Cl(3)–Ni–Cl(4)	80.81 (7)
N(1)–C(1)–C(2)	C(1)–C(2)–N(2)	14.12 (67)
N(1)–C(3)–C(4)	C(3)–C(4)–N(2)	12.66 (66)
N(1)–C(5)–C(6)	C(5)–C(6)–N(2)	14.06 (63)
N(1)–C(1)–C(2)	N(1)–C(3)–C(4)	118.69 (62)
N(1)–C(1)–C(2)	N(1)–C(5)–C(6)	118.31 (62)
N(1)–C(3)–C(4)	N(1)–C(5)–C(6)	117.71 (59)
N(2)–C(2)–C(1)	N(2)–C(4)–C(3)	117.20 (58)
N(2)–C(2)–C(1)	N(2)–C(6)–C(5)	118.36 (58)
N(2)–C(4)–C(3)	N(2)–C(6)–C(5)	119.10 (58)

[a] Primed atoms are related to unprimed atoms by a center of inversion at the origin.

Table IX. Geometrical Properties of Chlorine-Bridged Four-Membered Ring System

	Compound	M–Cl–M, Å	M–Cl, Å	Cl–Cl, Å	Ref
1.	$BeCl_2$	82.0	2.02	3.05	*a*
2.	$GaCl_3$	86.0	2.29	3.35	*b*
3.	$Al(CH_3)Cl_2$	91.1	2.26	3.15	*c*
4.	$[Co(NO)_2Cl]_2$	92.0	2.13, 2.33	3.12	*d*
5.	$[PdCl_2]_n$	93.0	2.31	3.18	*e*
6.	$[AuCl_3]_2$	94.0	2.34	3.18	*f*
7.	$[CuCl_2CH_3CN]_2$	94.0	2.30	3.14	*g*
8.	$[C_8H_{12}RhCl]_2$	95.0	2.38	3.22	*h*
9.	$[PtCl_2P(C_3H_7)_3]_2$	96.4	2.425, 2.315	3.16	*i*
10.	Mo_2Cl_{10}	98.6	2.53	3.30	*j*
11.	Re_2Cl_{10}	98.7	2.465	3.21	*k*
12.	Ni_2Cl_8	99.1	2.366, 2.449	3.12	*l*
13.	$(ClN)_2V_2Cl_6$	99.8	2.383, 2.463	3.12	24
14.	$[NbCl_3O]_2$	101.1	2.53	3.21	*m*
15.	$[TiCl_4POCl_3]_2$	101.2	2.44, 2.54	3.15	*n*
16.	Nb_2Cl_{10}	101.3	2.555	3.22	*o*
17.	$Ti_2Cl_{10}^{2-}$	101.5	2.481, 2.506	3.17	*p*

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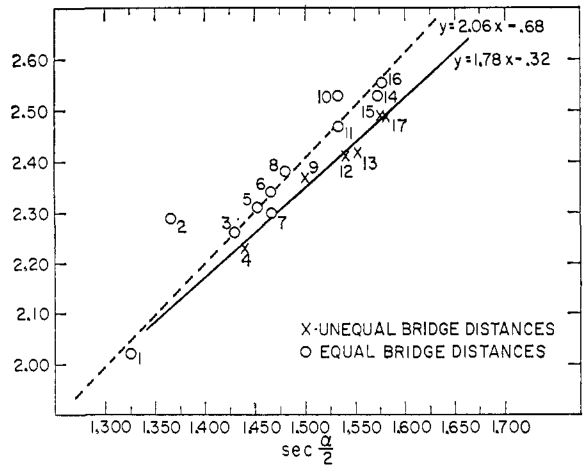

Figure 4. Metal–chlorine bond lengths plotted as a function of the secants of one-half the metal–chlorine–metal bridge angle. The open circles represent four-membered ring systems with opposite bond lengths equal, but unequal to adjacent bond lengths.

3.17 Å with a minimum Cl–Cl distance of 3.05 Å in $BeCl_2$ and a maximum distance of 3.30 Å in Mo_2Cl_{10}. Again with the exception of $[GaCl_3]_2$, the M–Cl–M bridge angle can be estimated to within 2° by the least-squares fit of two straight lines to the two sets of data.

The asymmetric bridge systems were treated by taking the average of the bridge metal–chlorine distances for the value of MB. Unequal bridge distances are observed primarily in first-row transition metal species with metal atoms in high formal oxidation states, such as $Ti_2Cl_{10}^{2-}$ and $(ClN)_2V_2Cl_6$, or in systems in which the metal–metal interaction is expected to be strongly antibonding, as in $(Co(NO)_2Cl)_2$. In the asymmetric bridge systems in Figure 4, the chlorine–chlorine distances range from 3.12 to 3.16 Å, strongly suggesting that 3.14 ± 0.02 Å represents an optimum closest approach. A tentative explanation for the asymmetry as defined above is that charges associated with the metal atoms force the metal atoms apart, and the M–Cl–M bridge angle opens until the "optimum" Cl–Cl distance is obtained. If the repulsion between the electronic charges associated with the metal atoms is sufficiently large, further separation of the metal centers is obtained by separating the species which are associated through the chlorine bridges.

The above analysis clearly indicates that to a first approximation, the chlorine-bridged four-membered ring geometries are determined by Cl–Cl intraring nonbonded forces. This is in distinct contrast to analogous amino-bridged species in which, over a similar variation in metal–bridge bond lengths (0.50 Å), bridge angles vary by only 3.0°.[29]

The coordination number of the metal atom is of secondary importance in chlorine-bridged species. The nature of other groups coordinated to the metal atom also appears to be relatively unimportant with the exception of the nickel and palladium olefinic systems. The M–Cl–M angles in $Pd_2Cl_2(H_2C{=}CH_2)_2$,[30] $[\pi\text{-}C_3H_5PdCl]_2$,[31] and $(C_8H_{12}NiCl_2)_2 \cdot C_6H_6$[32] are predicted by the

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empirical least-squares treatment of Figure 4 to be 97, 97, and 94°, respectively, while the observed values are 94, 92, and 92°. The Pd–bridge Cl bonds opposite the olefinic groups are 0.1 Å longer than the Pd–Cl bond lengths in $(PdCl_2)_n$. However, the ring angles in all three palladium compounds are the same. This observation can be rationalized by invoking the "*trans*" effect and requiring the palladium orbitals to be highly directional in character. This can be contrasted to the $Ni_2Cl_8^{4-}$ anion with a "well-behaved" Ni–Cl–Ni angle of 99.1°. $GaCl_3$ has a Ga–Cl–Ga angle approximately 5° less than that predicted by the Ga–Cl distance of 2.29 Å. Dahl[33] has pointed out that one of the factors leading to anomalously acute bridge angles is metal–metal bonding, and perhaps this is the case in $GaCl_3$.

The empirical nature of the least-squares fit is emphasized by the fact that the slopes are not equal to 1.58 Å, *i.e.*, 0.5 of the average Cl–Cl distance, and the intercepts are not equal to zero. Factors other than Cl–Cl repulsion undoubtedly become relatively more important at the extreme M–Cl distances (2.02 and 2.56 Å), such as inter-ring Cl–Cl repulsions in $[BeCl_2]_n$.

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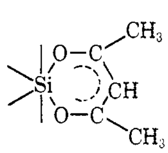
Triorganosilicon Acetylacetonates. Enol Ether Isomerism and Stereochemical Lability[1]

Thomas J. Pinnavaia, Ward T. Collins, and Jerry J. Howe

Contribution from the Department of Chemistry, Michigan State University, East Lansing, Michigan 48823. *Received February 17, 1970*

Abstract: Nuclear magnetic resonance studies of triorganosilicon acetylacetonates of the type $R(CH_3)_2Si(acac)$ ($R = n\text{-}C_4H_9$, C_2H_5, CH_3, $CH_2{=}CH$, $CF_3CH_2CH_2$, and C_6H_5), along with $(C_6H_5)_2(CH_3)Si(acac)$, show that the compounds possess an open-chain enol ether structure and give rise to configurations in which the uncoordinated carbonyl oxygen atom is positioned either *cis* or *trans* to the siloxy group. Equilibrium values of the *cis*-to-*trans* ratios in chlorobenzene are dependent on the nature of the substituents on silicon and lie in the range 0.25–0.39. The *cis* isomers undergo a rapid, intramolecular rearrangement process which interchanges the allylic and acetyl methyl groups on the acetylacetonate moiety. First-order rate constants for the stereochemical rearrangements were determined in chlorobenzene solution by nmr line-broadening techniques. In the *cis*-$R(CH_3)_2Si(acac)$ series of compounds, the lability increases in the order $R = n\text{-}C_4H_9 < C_2H_5 < CH_3 < CH_2{=}CH, C_6H_5 < CF_3CH_2CH_2$. The lability of *cis*-$(C_6H_5)_2(CH_3)Si(acac)$ is comparable to that of *cis*-$(CF_3CH_2CH_2)(CH_3)_2Si(acac)$. For the rearrangement of *cis*-$(CH_3)_3Si(acac)$, which was studied over the temperature range −36.2–38.4°, the values of the Arrhenius activation energy and frequency factor are 13.8 ± 0.5 kcal/mol and exp(13.05 ± 0.54), respectively. The kinetic data are consistent with a mechanism involving formation of a five-coordinated silicon intermediate. Some proton nmr chemical shift and mass spectral data are presented.

Silicon acetylacetonates[2] may adopt either a chelated (I) or an open-chain enol ether (II) structure, depending on the nature of the other substituents attached to the silicon atom. Neutral compounds of the type $RSi(acac)_2Cl$,[3] $Si(acac)_2(OCOR)_2$,[4,5] and probably $Si(acac)_2Cl_2$[6] have chelated ground-state structures in which silicon achieves a coordination number of six. When less electronegative substituents are present on silicon, as in compounds of the type $R_3Si(acac)$[3,7] or $R_2Si(acac)_2$,[3] four-coordinated silicon enol ether structures are attained.



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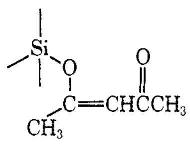

II

In an earlier communication from this laboratory[8] the existence of enol ether isomers for $(CH_3)_3Si(acac)$ was confirmed by nmr spectroscopy. Moreover, the isomer in which the uncoordinated carbonyl group is positioned *cis* to the siloxy group was shown to undergo a rapid intramolecular rearrangement process which interchanges the allylic and acetyl methyl groups on the acetylacetonate moiety. In the present study the kinetics of the rearrangement process has been investigated by nmr line-broadening techniques. Also, a series of new triorganosilicon acetylacetonates has been investigated in order to determine the dependence of the rearrangement rates on the polarity of the silicon substituents.

Experimental Section

Syntheses. All of the triorganosilicon acetylacetonates used in this study were prepared by reaction of stoichiometric amounts of

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(1) Presented in part before the Division of Inorganic Chemistry, 158th National Meeting of the American Chemical Society, New York, N. Y., Sept 1969.

(2) $CH_3COCHCOCH_3^-$, abbreviated acac.

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