

A Water Rich Crystalline Hydrate Formed by 1,4,7,10-Tetraazacyclododecane, Siliconhydrofluoric Acid and Water: Structure and Properties

MARINA S. FONARI,* YURII A. SIMONOV and VICTOR CH. KRAVTSOV
Institute of Applied Physics, Academy of Sciences of Moldova, Kishinev, Academy str. 5, 2028 Moldova.

VLADIMIR O. GELMBOLDT, EDWARD V. GANIN, YURII A. POPKOV and LARISA V. OSTAPCHUK
Institute of Environmental and Human Protection at Odessa State University, Odessa, 270100 Ukraine.

(Received: 18 December 1996; in final form: 1 May 1997)

Abstract. Novel complementary associations have been found in a crystalline ternary complex of the macrocyclic tetramine, [12]aneN₄ (e.g. = 1,4,7,10-tetraazacyclododecane, cyclen, L), hexafluorosilicate ions and water (**I**). The final compound belongs to the host–guest type with the macrocycle as the host (H), the inorganic entity as a guest (G) and water molecules. It was characterized by X-ray techniques, IR spectroscopy and thermogravimetric study. X-ray crystal analysis revealed that the structure is built of the charged entities, with a 3D-network uniting the quadriprotonated form of the macrocycle, hexafluorosilicate as counterions and lattice water molecules *via* N—H⁺ ··· F⁻, N—H⁺ ··· O(w), OH ··· F⁻ and O—H(w) ··· O(w) hydrogen bonds. The overall complex stoichiometry comprises four SiF₆²⁻ anions and seven water molecules per two [LH₄]⁴⁺ cations. Crystals of (**I**) are monoclinic, space group *P*2₁/*n* with *a* = 14.585(3), *b* = 16.384(2), *c* = 16.500(3) Å, β = 92.84(3)°, *V* = 3938(1) Å³ and *Z* = 8 for C₈H₃₁F₁₂N₄O_{3,5}Si₂.

Key words: Tetraazamacrocycle, host–guest complementarity, inclusion compound, H-bonds.

Supplementary Data relevant to this paper have been deposited with the British Library as Supplementary Publication No. sup 82229 (14 pages) and include: tables of H-atomic coordinates and their equivalent isotropic temperature factors, anisotropic temperature factors, a listing of observed and calculated structural factors.

1. Introduction

Macrocyclic polyamines are useful and versatile in coordination, bioinorganic, biomimetic and catalytic chemistry. There has been increasing interest in the chemistry of tetraazamacrocyclic metallic complexes since the 1960's. These N-containing macrocycles possess the ability to stabilize unusual oxidation states of the coordinated metals, which may be profoundly affected by the macrocyclic cavity size

* Author for correspondence.

[1–4]. On the other hand, the only known host–guest complexes of [12ane]N₄ are its trihydrate [5] and tetrahydrochloride [6].

In the course of our work on inclusion complexes between siliconhydrofluoric acid (H₂SiF₆) hydrolysis products and macrocycles, we have recently studied the structures of the inclusion compounds obtained with 18-crown-6, monoaza-18-crown-6, diaza-18-crown-6, diaza-15-crown-5 (as the host) with *trans*-diaquatetrafluorosilicate dihydrate [(*trans*-SiF₄·2H₂O)] [7], pentafluorosilicate monohydrate [(SiF₅·H₂O)][−] [8], hexafluorosilicate SiF₆^{2−} [9] (as the guest) as the result of the recognition process of the macrocycle in the aqueous solution of H₂SiF₆. The final complex obtained depends strictly on the set of N, O macrocyclic binding sites and the ring dimensions.

The macrocyclic tetramine, [12]aneN₄(= 1,4,7,10-tetraazacyclododecane, cyclen, L), was chosen for further selective extraction research in solution. Complex (I) has been investigated with respect to its solid state structure formation, spectroscopy and thermogravimetry. This detailed characterization provides the basis for an exploration of the mode of specific SiF₆^{2−} anion recognition and contributions of hydrogen bonding. Being the formal analogue of 12-crown-4, cyclen is interesting because its four NH sites are available for protonation in acidic medium, which predetermines the opportunity for another stoichiometry and host–guest complex architecture in comparison with the previously described compounds [7–9].

The structure of the complex stabilized in the form of a host–guest type compound has been established by X-ray analysis for the first time.

2. Experimental

2.1. SYNTHESIS OF COMPLEX (I)

A solution of 172 mg (1 mmol) of [12]aneN₄ in 10 mL of methanol was added to 0.5 mL (~5 mmol) of 45% siliconhydrofluoric acid. The mixture was heated on a water bath until the crystalline product formed. Crystals of the complex, suitable for X-ray investigation, were obtained by recrystallization from 15 mL of distilled water at its simultaneous evaporation. Colourless transparent crystals (I) soluble in methanol, benzene, hexane, acetone. *Anal. Calcd.* for C₁₆H₆₂F₂₄N₈O₇Si₄, Si 10.73; F 43.56. *Found*, % Si 10.45; F 44.91.

IR absorption spectra were recorded on a Specord 75 *IR* spectrophotometer (range 4000–400 cm^{−1}, samples as suspensions in Nujol mulls between KRS-5 windows).

Thermogravimetric analysis (TGA) was carried out on a OD-102 F. Paulik–J. Paulik–L. Erdey derivatograph in air (platinum crucible, Al₂O₃ internal standard, samples 50–70 mg, at a scanning heating rate of 10°/min. The sensitivity of DTA and DTG is 0.1 of the maximum.

Mass spectra were recorded on a Varian MAT-112 mass-spectrometer. (I) was directly introduced into the ion source. The ionizing energy was 70 eV. The peaks registered have been assigned to the SiF₃⁺ ion (*m/z* = 85) with maximum intensity

(13%) and the doubly protonated molecular ion M^{2+} of [12ane]N₄ ($m/z = 174$, $I = 11\%$).

2.2. X-RAY DATA COLLECTION, STRUCTURE DETERMINATION AND REFINEMENT

A colourless prismatic habitus crystal of **(I)** ($0.6 \times 0.4 \times 0.3$ mm) was used for the investigation. The crystal structure was determined from data collected on a DAR-UMB diffractometer with graphite-monochromated CuK_{α} radiation at room temperature. Lattice constants were refined by least squares fits of 25 reflections in the θ range 12.0 – 18.2° . The intensities were corrected for Lp factors but no absorption was taken into account. Three standard reflections were measured every hour and showed no crystal decay during data collection. An initial structural model was obtained by direct methods, and the nonhydrogen atoms were refined anisotropically. All hydrogen atoms were located on the electron density map. After that C-bound and N-bound H-atoms were moved to the idealized positions and refined in a ‘ride’ mode. The positions of O-bound H-atoms were refined isotropically. Full-matrix least squares refinement converged at $R_1 = 0.0713$ for 4910 independent reflections. Calculations were performed using SHELXS-86 [10] (structure solution), SHELXL-93 [11] (structure refinement) and PARST-95 [12] (H-bond calculation) crystallographic software packages. Two crystallographically independent quadriprotonated macrocyclic cations [LH₄]⁴⁺, four SiF₆²⁻ anions and seven water molecules are in the asymmetric unit. By an inspection of the difference Fourier map it was found that one of the hexafluorosilicate anions (numerical indices 21–26) is disordered at two close locations. The refinement of two positions showed that they are distinguished only by their orientation and the two sites for the Si atoms practically coincide (Si(2)—Si(2)# distance is 0.134 \AA). Anion atoms were given two alternative positions with approximately the same occupancy factors of 0.54(2) and 0.46(2) respectively. Only one position for this disordered entity is shown in the figures for clarity. The crystal data and data collection parameters are displayed in Table I. Fractional atomic coordinates, bond distances, valent and torsion angles of the asymmetric unit are given in Tables II and III respectively.

3. Discussion

3.1. OVERALL SYSTEM OF HOST–GUEST INTERACTIONS IN **(I)**

The content of the unit cell independent part with the host : guest : water component ratio $2 : 4 : 7$ is depicted in Figure 1. Close intermolecular contacts are listed in Table IV. Each of the four N-atoms in two cyclen entities (denoted as **a** and **b**) have acquired additional protons and hence the rings exist as quadriprotonated cations with all $>NH_2^+$ protons oriented outwardly resembling those in the structure of the cyclen tetrahydrochloride, [LH₄]Cl₄ [6]. Thus, the crystal comprised of positively charged macrocycles, negatively charged hexafluorosilicate anions and a number

Table I. Crystal data and structure refinement for **(I)**.

Compound	Complex (I)
Empirical formula	C ₈ H ₃₁ F ₁₂ N ₄ O _{3.5} Si ₂
Formula weight	523.55
Temperature/K	293(2)
Radiation, λ/Å	CuK _α , 1.5418
Crystal system	Monoclinic
<i>a</i> /Å	14.585(3)
<i>b</i> /Å	16.384(2)
<i>c</i> /Å	16.500(3)
β/°	92.84(3)
<i>V</i> /Å ³	3938(1)
<i>Z</i>	8
<i>D</i> _{calc} /g cm ⁻³	1.766
μ/cm ⁻¹	2.928
<i>F</i> (000)	2168
Crystal dimensions/mm	0.60 × 0.40 × 0.30
θ range for data collection/°	3.80 < θ < 70.48
Index ranges	-16 < <i>h</i> < 0 0 < <i>k</i> < 20 -19 < <i>l</i> < 20
Reflections collected	5030
Independent reflections	4945 [<i>R</i> (int) = 0.0063]
Refinement method	Full-matrix least-squares on <i>F</i> ²
<i>a</i> , <i>b</i> in weighting scheme	0.1513, 8.7472
Data/restraints/parameters	4910/36/654
Goodness-of-fit on <i>F</i> ²	1.055
Final <i>R</i> indices [<i>I</i> > 2σ(<i>I</i>)]	<i>R</i> ₁ = 0.0713, <i>wR</i> ₂ = 0.1925
<i>R</i> indices (all data)	<i>R</i> ₁ = 0.0732 <i>wR</i> ₂ = 0.2045
Large diff. peak and hole/e Å ⁻³	0.779 and -0.792

Weighting scheme $w = 1/[\sigma^2(F_0^2) + (aP)^2 + bP]$, where $P = (F_0^2 + 2F_0^2)/3$.

of lattice water molecules possesses numerous possibilities for reciprocal binding saturation.

The environment of the two independent [LH₄]⁴⁺ entities has both common features and differences as shown in Figure 2. They exhibit an inclination to bind negatively charged species by means of NH⁺⋯F⁻ hydrogen bonds, either classic or bifurcated in nature. In **(I)** the ion-pair formation arises from electrostatic interaction and hydrogen bonding of the NH⁺⋯F⁻ type in a rather similar manner with [LH₄]Cl₄ [6] and complexes of protonated hexaaza-18-crown-6 [13–15], where NH⁺⋯O⁻ interactions stabilize the corresponding complexes. In **(I)** both macrocycles (**a**, **b**) use all opportunities for NH⋯acceptor interactions: each of them is surrounded by SiF₆²⁻ counterions, serving as the bridges to unite structural units in a 3D arrangement. Four out of the seven water molecules incorporated

Table II. Atomic coordinates ($\times 10^4$) and equivalent isotropic displacement parameters ($\text{\AA}^2 \times 10^3$) for **(I)**. $U(\text{eq})$ is defined as one third of the trace of the orthogonalized U_{ij} tensor (e.s.d.s are in parentheses).

Si(1)	9602(1)	2611(1)	1595(1)	21(1)
F(11)	10715(2)	2310(2)	1663(2)	26(1)
F(12)	9577(2)	2627(2)	2606(2)	37(1)
F(13)	9614(2)	2597(2)	584(2)	39(1)
F(14)	9251(2)	1637(2)	1587(2)	30(1)
F(15)	9942(2)	3589(2)	1587(2)	38(1)
F(16)	8489(2)	2909(2)	1535(2)	34(1)
Si(2)	7009(4)	4430(3)	3554(3)	22(2)
F(21)	6620(7)	3472(4)	3692(7)	37(3)
F(22)	7408(7)	5377(4)	3420(6)	51(4)
F(23)	7704(11)	4333(9)	4389(7)	112(7)
F(24)	7837(8)	4051(5)	2990(10)	97(6)
F(25)	6319(9)	4516(7)	2718(6)	82(5)
F(26)	6176(10)	4790(7)	4113(9)	91(6)
Si(2#)	6977(5)	4384(5)	3614(4)	36(3)
F(21#)	6536(8)	3476(6)	3882(8)	49(4)
F(22#)	7424(9)	5283(7)	3350(7)	84(7)
F(23#)	7256(11)	4582(7)	4590(4)	74(5)
F(24#)	8002(6)	3934(7)	3525(13)	84(7)
F(25#)	6700(13)	4176(13)	2641(4)	132(9)
F(26#)	5951(6)	4818(8)	3712(12)	85(6)
Si(3)	3183(1)	921(1)	3582(1)	23(1)
F(31)	2710(3)	64(2)	3917(2)	48(1)
F(32)	3745(2)	343(2)	2911(2)	34(1)
F(33)	2307(3)	1050(2)	2890(2)	47(1)
F(34)	4083(3)	793(2)	4255(2)	49(1)
F(35)	3698(3)	1754(2)	3221(3)	56(1)
F(36)	2642(3)	1467(2)	4261(2)	45(1)
Si(4)	5018(1)	3118(1)	675(1)	19(1)
F(41)	6101(2)	2781(2)	781(2)	35(1)
F(42)	3932(2)	3431(2)	517(2)	35(1)
F(43)	4785(2)	2777(2)	1605(2)	34(1)
F(44)	4707(3)	2201(2)	282(2)	41(1)
F(45)	5255(2)	3448(2)	-259(2)	44(1)
F(46)	5304(3)	4023(2)	1080(2)	46(1)
N(1a)	1849(3)	3593(2)	2129(2)	24(1)
C(2a)	2850(4)	3370(3)	2104(3)	26(1)
C(3a)	3454(4)	4109(3)	2312(3)	24(1)
N(4a)	4328(3)	3915(3)	2770(2)	26(1)
C(5a)	4257(4)	3577(3)	3614(3)	27(1)
C(6a)	3885(4)	4220(3)	4177(3)	26(1)
N(7a)	3658(3)	3855(3)	4972(2)	26(1)
C(8a)	2848(4)	3300(3)	4992(3)	30(1)
C(9a)	1939(4)	3721(4)	4792(3)	30(1)

Table II. Continued.

N(10a)	1280(3)	3193(3)	4308(3)	30(1)
C(11a)	1517(4)	2987(3)	3467(3)	27(1)
C(12a)	1484(4)	3743(3)	2948(3)	24(1)
N(1b)	8889(3)	524(2)	4032(3)	25(1)
C(2b)	8172(4)	132(3)	4535(3)	27(1)
C(3b)	7657(4)	-538(3)	4062(3)	29(1)
N(4b)	6651(3)	-561(3)	4212(3)	27(1)
C(5b)	6068(4)	157(3)	3983(3)	34(1)
C(6b)	5988(4)	272(3)	3072(3)	31(1)
N(7b)	5518(3)	1060(3)	2854(3)	35(1)
C(8b)	6037(4)	1828(3)	3035(4)	32(1)
C(9b)	6873(4)	1933(3)	2512(3)	30(1)
N(10b)	7668(3)	2309(2)	2967(3)	26(1)
C(11b)	8116(4)	1827(3)	3657(3)	25(1)
C(12b)	8539(4)	1057(3)	3351(3)	26(1)
O(1w)	4787(4)	838(3)	1295(3)	52(1)
O(2w)	2876(4)	579(3)	1348(3)	50(1)
O(3w)	2695(3)	1981(3)	346(3)	48(1)
O(4w)	1422(4)	3261(3)	141(3)	59(1)
O(5w)	437(3)	580(3)	2469(3)	53(1)
O(6w)	5607(4)	3899(4)	5370(4)	74(2)
O(7w)	9777(4)	4231(3)	4128(4)	71(2)

in the structure (O(1w), O(5w), O(6w), O(7w)) are involved in cooperation with $>\text{NH}_2^+$ binding sites by one of their lone pairs. Nevertheless, three of them (O(5w), O(6w), O(7w)) approach one macrocycle (**a**), while only one O(1w) approaches the other (**b**, Figure 2). In turn, all guest counterions also use their vacancies for $\text{NH}\cdots\text{F}$ and $\text{OH}\cdots\text{F}$ interactions.

Of particular interest in this crystal, grown from aqueous solution and containing charged species, is the fact of inclusion in the lattice of water molecules in the form of a linear cluster of five distinctive water molecules in a sequence: O(7w) \cdots O(1w) \cdots O(2w) \cdots O(3w) \cdots O(4w) *via* strong hydrogen bonds involving both H-atoms and lone pairs in cooperation (Figure 3). These united water molecules fill the voids in the 3D network built of the spacious charged entities and provide their additional binding. Two remaining water molecules interact separately only with macrocyclic cations and inorganic anions. The utilization of the hydrogen bonding potential of the water of crystallization is very high.

Besides the abovementioned $\text{N}-\text{H}^+\cdots\text{F}^-$, $\text{N}-\text{H}^+\cdots\text{O}(\text{w})$, $\text{OH}\cdots\text{F}^-$ and $\text{O}-\text{H}(\text{w})\cdots\text{O}(\text{w})$ hydrogen bonds, numerous $\text{C}-\text{H}\cdots\text{F}$ interactions are present in the crystal with $\text{C}\cdots\text{F}$ and $\text{H}(\text{C})\cdots\text{F}$ distances in the ranges 3.129(6)–3.323(6) and 2.31–2.40 Å, respectively.

Table III. Distances (Å) and angles (°) for **(I)** (e.s.d.s are in parentheses).

	$n = 1$	$n = 2$	$n = 2\#$	$n = 3$	$n = 4$
Si(n)—F(n1)	1.695(3)	1.689(4)	1.689(4)	1.671(3)	1.673(3)
Si(n)—F(n2)	1.671(3)	1.675(4)	1.676(4)	1.698(3)	1.673(3)
Si(n)—F(n3)	1.669(3)	1.676(4)	1.673(4)	1.683(4)	1.683(3)
Si(n)—F(n4)	1.676(3)	1.680(4)	1.680(4)	1.691(4)	1.689(3)
Si(n)—F(n5)	1.678(3)	1.674(4)	1.672(4)	1.681(4)	1.685(3)
Si(n)—F(n6)	1.694(3)	1.669(4)	1.672(4)	1.663(3)	1.671(3)
F(n2)—Si(m)—F(n1)	90.4(2)	179.3(3)	179.5(4)	88.1(2)	176.8(2)
F(n3)—Si(m)—F(n1)	90.3(2)	89.7(3)	89.8(3)	91.0(2)	91.6(2)
F(n4)—Si(m)—F(n1)	90.8(2)	89.2(2)	89.3(3)	89.9(2)	89.0(2)
F(n5)—Si(m)—F(n1)	89.8(2)	89.7(3)	89.7(3)	177.0(2)	88.1(2)
F(n6)—Si(m)—F(n1)	179.5(2)	89.7(3)	89.7(3)	90.7(2)	92.0(2)
F(n3)—Si(m)—F(n2)	179.3(2)	89.8(3)	90.1(3)	90.2(2)	90.6(2)
F(n4)—Si(m)—F(n2)	90.1(2)	90.3(3)	90.2(3)	88.5(2)	88.7(2)
F(n3)—Si(m)—F(n4)	90.8(2)	90.7(3)	90.4(3)	89.0(2)	89.7(2)
F(n2)—Si(m)—F(n5)	89.1(2)	90.7(2)	90.7(3)	178.2(2)	90.3(2)
F(n3)—Si(m)—F(n5)	89.9(2)	89.9(3)	89.7(3)	178.4(2)	89.6(2)
F(n4)—Si(m)—F(n5)	89.3(2)	179.3(3)	179.4(4)	89.8(2)	179.4(2)
F(n2)—Si(m)—F(n6)	90.2(2)	90.4(3)	90.0(3)	91.1(2)	89.3(2)
F(n3)—Si(m)—F(n6)	179.0(2)	89.6(3)	90.0(3)	89.2(2)	89.9(2)
F(n4)—Si(m)—F(n6)	89.0(2)	178.9(3)	179.0(3)	90.2(2)	178.5(2)
F(n5)—Si(m)—F(n6)	90.4(2)	90.1(3)	90.3(3)	92.1(2)	91.2(2)

Table III. Continued.

	a		b		a		b	
N(1)—C(12)	1.497(6)		1.492(6)		C(12)—N(1)—C(2)	116.8(4)	116.5(4)	
N(1)—C(2)	1.507(7)		1.510(7)		N(1)—C(2)—C(3)	110.6(4)	111.3(4)	
C(2)—C(3)	1.526(7)		1.524(7)		N(4)—C(3)—C(2)	114.7(4)	113.5(4)	
C(3)—N(4)	1.484(7)		1.500(7)		C(3)—N(4)—C(5)	116.8(4)	119.4(4)	
N(4)—C(5)	1.507(6)		1.489(7)		N(4)—C(5)—C(6)	110.5(4)	111.5(4)	
C(5)—C(6)	1.522(7)		1.513(7)		N(7)—C(6)—C(5)	111.1(4)	111.0(4)	
C(6)—N(7)	1.494(6)		1.498(7)		C(6)—N(7)—C(8)	118.1(4)	116.9(4)	
N(7)—C(8)	1.493(7)		1.491(7)		N(7)—C(8)—C(9)	113.8(4)	113.3(5)	
C(8)—C(9)	1.516(8)		1.538(8)		N(10)—C(9)—C(8)	112.5(5)	112.6(4)	
C(9)—N(10)	1.495(7)		1.483(7)		C(11)—N(10)—C(9)	117.1(4)	117.6(4)	
N(10)—C(11)	1.485(7)		1.507(6)		N(10)—C(11)—C(12)	110.2(4)	110.9(4)	
C(11)—C(12)	1.506(6)		1.502(7)		N(1)—C(12)—C(11)	112.3(4)	111.8(4)	
C(12)—N(1)—C(2)—C(3)	-71.5(5)		71.5(5)					
N(1)—C(2)—C(3)—N(4)	145.5(4)		-141.2(4)					
C(2)—C(3)—N(4)—C(5)	-65.5(5)		62.3(6)					
C(3)—N(4)—C(5)—C(6)	-67.4(6)		67.0(6)					
N(4)—C(5)—C(6)—N(7)	170.1(4)		-171.7(4)					
C(5)—C(6)—N(7)—C(8)	-70.6(6)		70.8(7)					
C(6)—N(7)—C(8)—C(9)	-65.6(6)		67.5(6)					
N(7)—C(8)—C(9)—N(10)	143.0(4)		-142.9(4)					
C(8)—C(9)—N(10)—C(11)	-67.1(6)		65.9(6)					
C(9)—N(10)—C(11)—C(12)	-67.0(6)		64.2(6)					
N(10)—C(11)—C(12)—N(1)	171.7(4)		-173.2(4)					
C(11)—C(12)—N(1)—C(2)	-64.4(6)		69.0(6)					

Table IV. Geometric parameters of hydrogen bonds in (I).

Donor—H—Acceptor	D—H, Å	D···A, Å	H···A, Å	D—H···A, °
N(1a)—H(1a)···F(31 ²)	0.90	3.051(5)	2.24	150
N(1a)—H(1a)···F(32 ²)	0.90	2.996(5)	2.29	135
N(1a)—H(1b)···F(11 ¹)	0.90	2.760(5)	1.88	165
N(4a)—H(4a)···O(5w ²)	0.96	2.780(6)	1.99	139
N(4a)—H(4b)···F(43)	0.96	2.782(5)	1.88	155
N(7a)—H(7a)···F(26 ³)	0.90	2.69(1)	1.83	158
N(7a)—H(7a)···F(26# ³)	0.90	3.11(1)	2.27	153
N(7a)—H(7b)···F(13 ⁴)	0.90	2.914(5)	2.14	144
N(7a)—H(7b)···O(6w)	0.90	2.887(8)	2.20	133
N(10a)—H(10a)···F(41 ⁴)	0.90	2.931(6)	2.16	143
N(10a)—H(10b)···O(7w ¹)	0.90	2.778(7)	1.90	163
N(1b)—H(1c)···F(46 ⁵)	0.96	2.736(5)	1.88	147
N(1b)—H(1d)···F(45 ⁷)	0.96	2.820(6)	1.90	161
N(4b)—H(4c)···F(16 ⁵)	0.90	2.797(5)	1.97	152
N(4b)—H(4d)···F(34 ⁸)	0.90	2.822(6)	1.98	155
N(7b)—H(7c)···O(1w)	0.90	2.759(7)	1.88	164
N(7b)—H(7d)···F(32)	0.90	2.846(6)	2.20	128
N(7b)—H(7d)···F(35)	0.90	2.977(7)	2.20	144
N(10b)—H(10c)···F(21a)	0.90	2.773(9)	1.95	151
N(10b)—H(10c)···F(21b)	0.90	2.94(1)	2.13	151
N(10b)—H(10d)···F(16)	0.90	2.875(5)	2.06	151
O(1w)—H(1w1)···F(44)	0.95	2.791(5)	1.88	160
O(1w)—H(2w1)···O(2w)	0.95	2.824(8)	1.88	180
O(2w)—H(1w2)···F(32)	1.00	2.845(5)	1.98	143
O(2w)—H(1w2)···F(33)	1.00	2.826(6)	1.97	143
O(2w)—H(2w2)···O(3w)	0.95	2.834(6)	2.27	118
O(3w)—H(1w3)···F(44)	0.95	2.967(6)	2.03	166
O(3w)—H(2w3)···F(23a ⁹)	1.00	2.62(1)	1.64	167
O(3w)—H(2w3)···F(23b ⁹)	1.00	2.931(9)	1.94	169
O(4w)—H(1w4)···F(13 ¹)	0.95	2.984(6)	2.10	154
O(4w)—H(2w4)···O(3w)	0.95	2.806(7)	1.93	153
O(5w)—H(1w5)···F(33)	0.95	2.882(6)	2.05	145
O(5w)—H(2w5)···F(14 ¹)	0.95	2.810(6)	2.19	122
O(6w)—H(1w6)···F(11 ⁴)	1.18	2.909(7)	1.88	143
O(6w)—H(1w6)···F(13 ⁴)	1.18	2.880(7)	2.21	113
O(6w)—H(2w6)···F(21b)	1.13	3.010(10)	2.04	141
O(6w)—H(2w6)···F(26a)	1.13	2.650(10)	1.92	119
O(6w)—H(2w6)···F(23b)	1.13	3.080(10)	2.07	147
O(7w)—H(1w7)···O(1w ⁶)	0.95	2.808(7)	1.87	170
O(7w)—H(2w7)···F(24b)	0.95	2.775(9)	1.90	152

Symmetry codes: (1) $x, -1, +y, +z$, (2) $-x + 1/2, +y + 1/2, -z + 1/2$, (3) $-x + 1, -y + 1, -z + 1/2$, (4) $x - 1/2, -y + 1/2, +z + 1/2$, (5) $-x + 3/2, +y - 1/2, -z + 1/2$, (6) $x + 1/2, -y + 1/2, +z + 1/2$, (7) $x - 1/2, -y + 1/2, +z - 1/2$, (8) $-x + 1, -y, -z + 1$, (9) $-x + 3/2, +y + 1/2, -z + 1/2$.

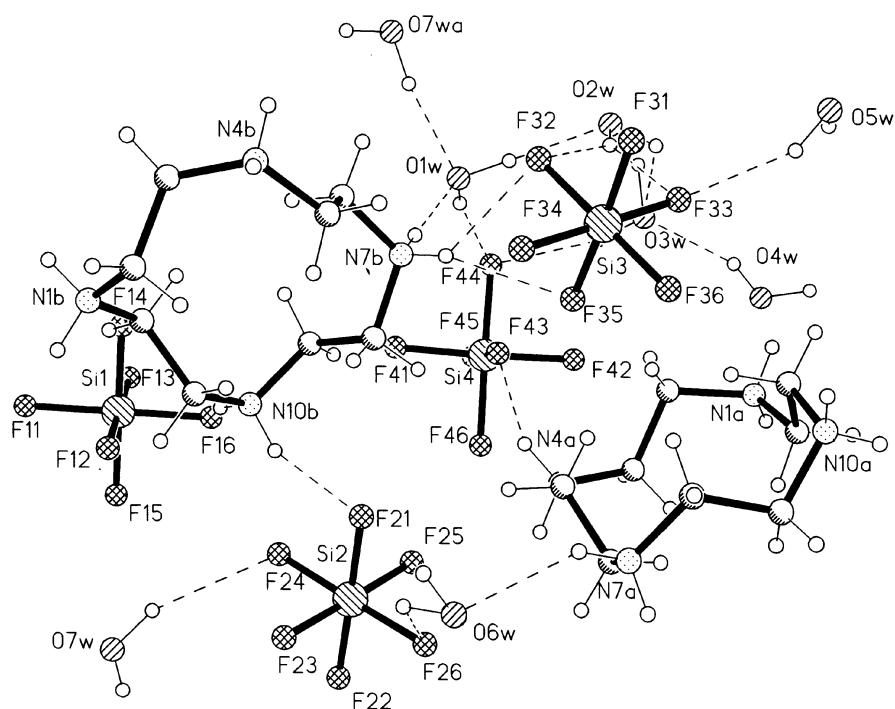


Figure 1. View of the unit cell independent part for complex (I) with H-bond description and partial atomic numbering scheme.

3.2. STRUCTURE OF INORGANIC MOIETIES

The geometric parameters of the doubly negatively charged hexafluorosilicate anions are similar between themselves and to those in other SiF_6^{2-} containing complexes [9, 16]. Si—F distances vary in the range 1.663(3)–1.698(3) Å. The tendency is evident: for each guest entity the longest Si—F distance corresponds to the strongest ion–ion $\text{NH}^+ \cdots \text{F}^-$ interaction. The $\text{F}^- \cdots \text{HO}$ hydrogen bond also elongates the Si—F distance, but to a lesser extent. The shortest Si—F distance, i.e., Si(3)—F(36) = 1.663(3) Å or Si(1)—F(12) = 1.671(3) Å corresponds to a fluorine atom not involved in H-bond interactions. Nevertheless, despite some deviation in Si—F distances, the silicon octahedral polyhedron still remains only slightly distorted (see Table III) and has approximate C_{4v} symmetry.

3.3. MACROCYCLE CONFORMATION AND GEOMETRY

The cyclen conformation in the complex is also of particular interest. It is important in understanding the effect of preorganization on complex stability and selectivity for metal ions and other species. Earlier works have described the conformation of the neutral cyclen entity in metal complexes. Due to the small ring size, [12]ane N_4

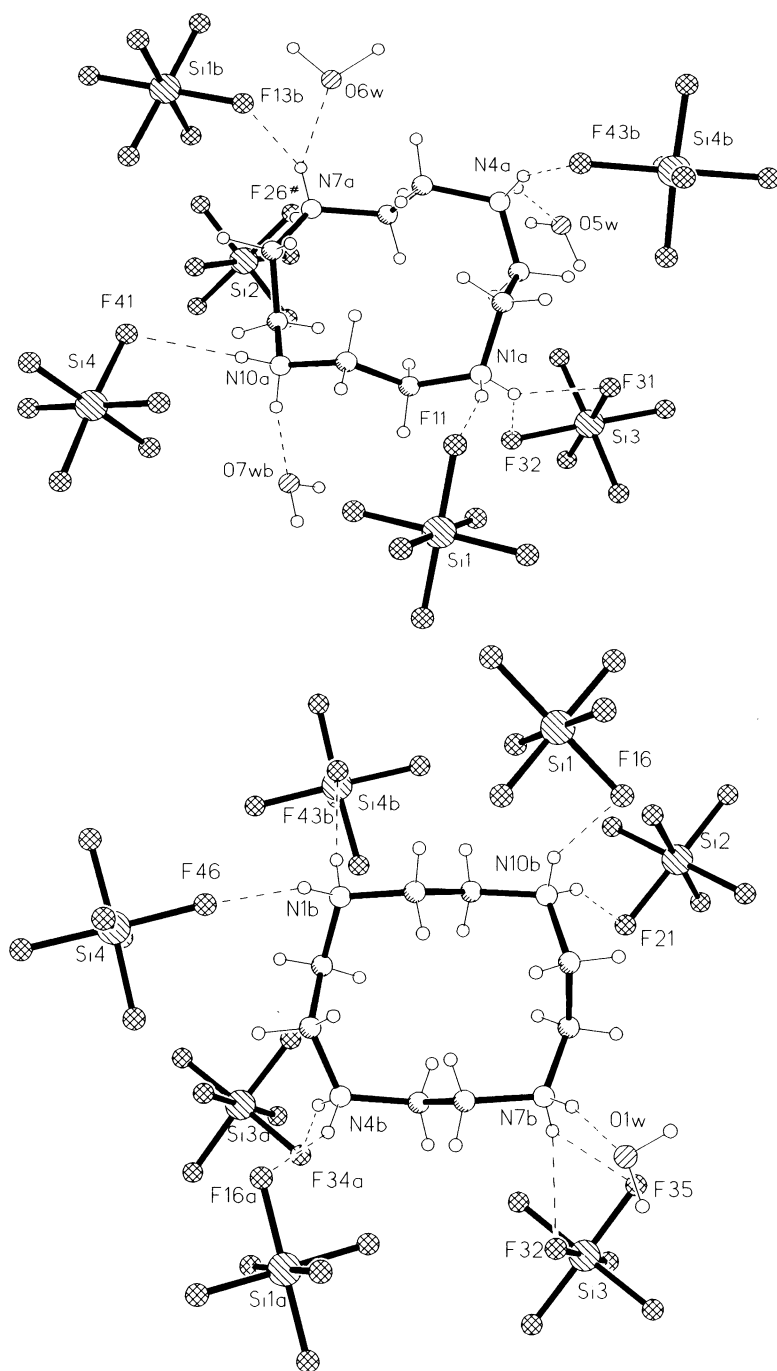


Figure 2. The nearest environment of the **a** and **b** cyclen entities in **(I)** with H-bond denotation. The letter notications mark guest entities connected with the corresponding basic ones by symmetry codes given in Table IV.

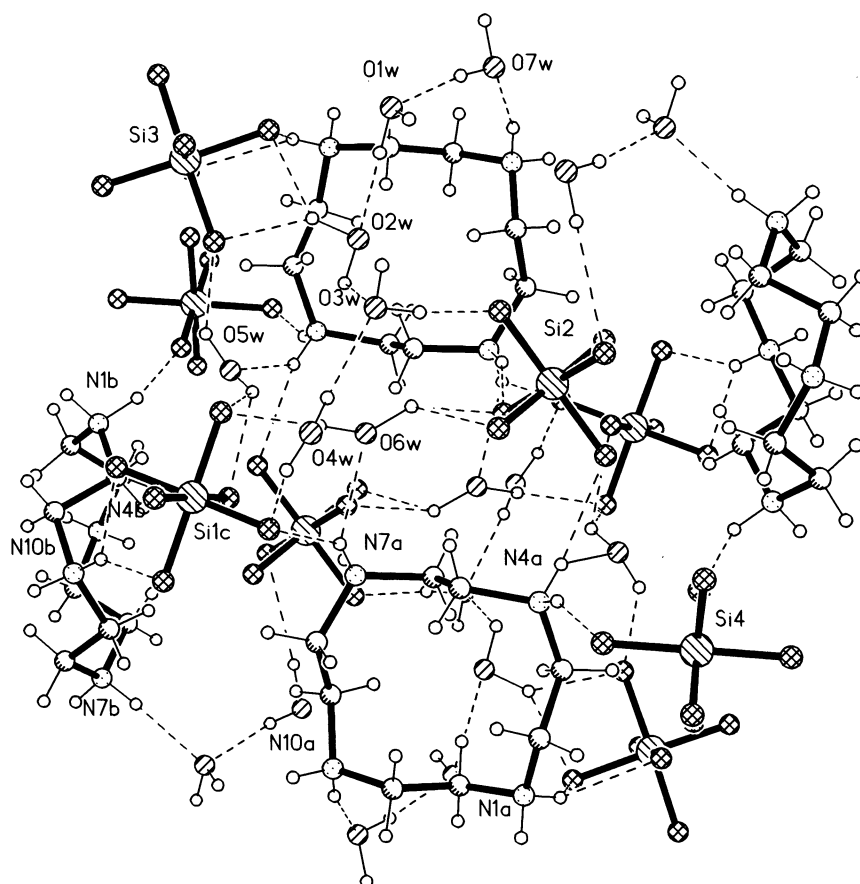


Figure 3. Fragment of crystal packing in (I).

coordinates to metals in a so-called folded or butterfly-like configuration. Three possible orientations of H-atoms attached to nitrogen atoms in respect to the plane of nitrogens in the macrocycle are available: all-*exo* (structure A); *exo, endo, exo, exo* (structure B); *exo, endo, exo, endo* (structure C). The crystal structures of octahedral Rh (II) [2], Cr(III) [4], Co(III) [17–19] and Ni(II) [20] show structure B. Another Ni(II) structure [3] exhibits cyclen in the A configuration. However no complex has yet been reported with cyclen in the C configuration.

Figure 4 depicts the structures of two independent ring molecules and the numbering scheme used. Previous works have shown that the neutral cyclen molecules in the cyclen trihydrate structure [5] exhibit crystallographic twofold rotational symmetry and have a [3333] quadrangular conformation in the crystalline state when the twelve-membered ring folds to form four repeating units, each containing two adjacent bonds with a *gauche* configuration and one bond with an *anti* configuration. This conformation, which establishes four ‘corner’ atoms, has been

labeled as the quadrangular [3333] conformation [21]. The [LH₄]⁴⁺ cation in the cyclen tetrahydrochloride complex [6] as in the present study also prefers the [3333] quadrangular conformation. The similar structures of the protonated [LH₄]⁴⁺ and cyclen entities differ in the position of the N atoms in the ring with respect to the side and corners of the conformation. For the cyclen cation, the N atoms are located at the corners of the square while for the neutral cyclen molecule the N atoms are located along the sides. The conformation changes are governed, perhaps, by the electrostatic (Coulombic) repulsions between positively charged N atoms. The distinctions are also seen in the orientation of N-bound hydrogen atoms. In neutral cyclen the H atoms bound to the N atoms at the 1 and 7 ring positions are directed outward, away from the center of the ring, the H atoms bound to the N atoms at the 4 and 10 ring positions are pointed inward, toward the center of the ring. In the quadriprotonated rings described here and as cited in [6] all >NH₂⁺ binding sites are oriented outwardly.

The average C—N distance is significantly shorter for the neutral molecule (1.464(3) Å [5]) than for the cation (1.497(3) Å in [6]), 1.496(7) Å (**a**), 1.494(6) Å (**b**) (present work).

This tendency is observed in hexaaza-18-crown-6 complexes [13] (C—N distances for the neutral molecule are 1.45–1.47(2), and for the protonated one they are 1.49–1.52(2) Å). The average C—C distances in the cyclen cation and neutral molecule [1.527(7) [6], 1.518(7) Å [5] and 1.517(7) Å (**a**), 1.519(7) Å (**b**) (this work)] do not differ significantly. The cation ring conformation is quite strained, as revealed in the increased values of all valent angles, especially those at N-corner atoms which are in the range 116.8(4)–118.1(4)° [116.5(4)–119.4(4)° for the **b**-molecule]. Both rings have a practically flat square-like shape with the equal deviations of the N-atoms from the average plane which is ± 0.143 Å.

3.4. IR SPECTROSCOPIC CHARACTERISTICS OF (**I**)

The IR data for complex (**I**) are reproduced in Table V together with the spectrum of the uncomplexed ether. Instead of the broad band of medium-weak intensity at 3300 cm⁻¹ and a shoulder at 3100 cm⁻¹ in the spectrum of [12]aneN₄, the IR spectrum in the N—H stretching mode for (**I**) in the range of 3625–3100 cm⁻¹ consists of a series of bands responsible for the ν(OH) stretching modes of lattice water (higher frequencies) and ν(NH) frequencies of NH₂⁺ groups. The δ(H₂O) and δ(NH₂) bending modes in the spectrum of (**I**) give multiple bands in the 1650–1565 cm⁻¹ range. The spectral features of (**I**) closely resemble those of the free macrocycle. The comparison of the two spectra in the range of interligand frequencies (1400–800 cm⁻¹) show that the protonated and neutral rings remain indistinguishable from the IR data. The corresponding band number, their positions and intensities remain practically invariable.

As far as the IR spectrum of (**I**) is concerned the most relevant features associated with the SiF₆²⁻ ligand are a strong ν(SiF) absorption band centered at 720

Table V. Observed wavenumbers (cm^{-1}) in the IR spectra of [12]aneN₄ and complex **(I)**.

[12]aneN ₄	(I)	Assignment
	3625 sh ^a	
	3565 s	
	3490 sh	
3300 m br	3425 sh	
3100 sh	3100 c	$\nu(\text{NH}), \nu(\text{OH})$
1650 sh	1650 sh	
1620 s		
1600 sh	1595 vs	
	1565 sh	$\delta(\text{H}_2\text{O}), \delta(\text{NH}_2)$
1330 w	1330 sh	
1300 m	1305 sh	
1270 m	1280 m	
1230 m	1230 m	
1180 w		$\omega(\text{CH}_2), \nu(\text{CN})$
1140 m	1140 m	
	1123 m	
1110 m	1110 sh	
1070 sh	1070 sh	
1050 s	1052 m	$\nu(\text{CC}), \tau(\text{CH}_2)$
1020 sh	1020 sh	
975 s	980 vs	
	965 m	
945 m	940 m	
910 m	900 vs	
	875 w	
830 m	825 sh	$\nu(\text{CC}), \nu(\text{CN}), \rho(\text{CH}_2)$
	745 sh	
	720 s	$\nu(\text{SiF})$
	640 sh	
550 sh	535 w	
	515 w	$\delta(\text{CCN}), \delta(\text{CNC})$
	475 s	
	430 sh	$\delta(\text{SiF}_2)$

^a sh = shoulder, s = strong, m = medium, v = very, w = weak, br = broad, respectively.

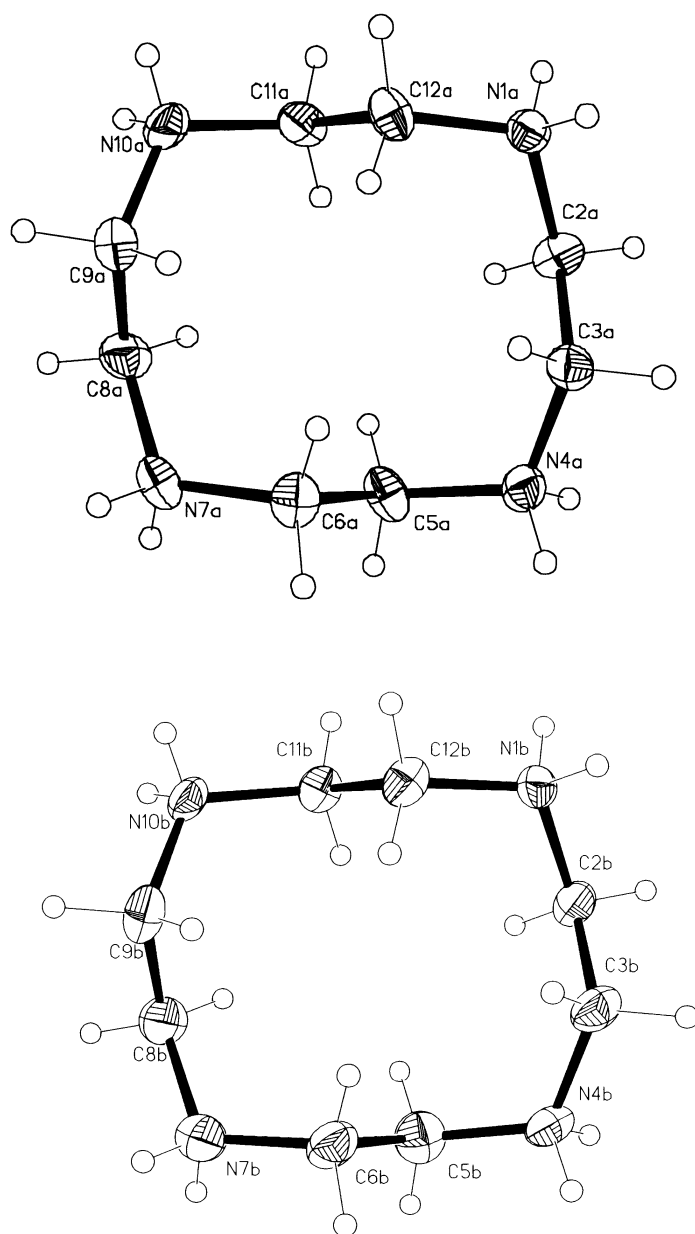


Figure 4. ORTEP view of macrocycles **a** and **b** in **(I)** with atomic numbering scheme.

cm^{-1} (with a shoulder at 745 cm^{-1}) and the $\delta(\text{SiF}_2)$ band at 475 cm^{-1} with a shoulder at 430 cm^{-1} . Comparatively small values of the splitting of degenerate frequencies of $\nu(\text{SiF})$ and $\nu(\text{SiF}_2)$ (F_{1u}) in the spectrum of **(I)** are connected with

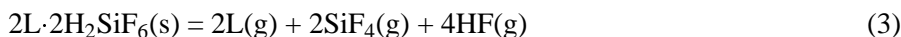
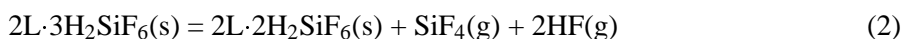
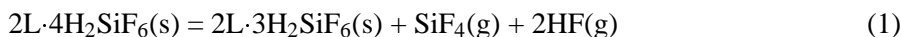
Table VI. Thermogravimetric data for (I).

Type	Effect		Weight loss		Assignment
	t_0 , °C	t_{\max} , °C	Found	Calcd	
<i>endo</i>	100	145	12.2	12.0	7 water molecules loss
<i>endo</i>	–	190	22.6	25.8	Decay according to (1)
<i>endo</i>	235	270	35.7	39.6	Decay according to (2)
<i>endo</i>	–	330	100	100	Decay according to (3)

some distortion of the SiF_6^{2-} anionic octahedral structure due to the fluoroligands involvement in the H-bond system.

3.5. THERMOGRAVIMETRIC STUDY

The thermogravimetric parameters related to complex (I) are reported in Table VI. Thermogravimetric analysis (TGA) indicates that the complex crystallizes as the heptahydrate where the thermal process has a weight loss corresponding to the number of water molecule estimated by the elemental analysis. The first stage of thermolysis points to the loss of water, found and calculated values for water loss during the dehydration being rather close. The weight loss of the sample on further heating is followed (Table VI, Scheme). By 190 °C about 23% of the sample weight has been lost and heating to 270 °C leads to a further loss of 36%. These changes correspond to the transformation of the anhydrous form of hexafluorosilicate and connected with the stage by stage removal of H_2SiF_6 in the form $\text{SiF}_4 + 2\text{HF}$ as in accordance with schemes (1–3):



4. Conclusion

The structure demonstrated here provides a new and complex example of the self-organization of many particles including a tetraazamacrocyle, inorganic entities, unique water molecules and water clusters. One may speculate that this complicated architecture driven by the interplay of different forces involved in the crystal engineering (electrostatic ones and various types of strong $\text{N}-\text{H}^+\cdots\text{F}^-$, $\text{N}-\text{H}^+\cdots\text{O}(\text{w})$, $\text{OH}\cdots\text{F}^-$ and $\text{O}-\text{H}(\text{w})\cdots\text{O}(\text{w})$ and weak $\text{C}-\text{H}\cdots\text{F}$ H-bonds). The ability of the water molecule to form clusters is well known [22–24]. The structure under discussion gives an additional example of the inclusion of a five-membered linear cluster in the ionic type network and the creation of diverse types of interactions.

We conclude that hydrogen bonds between SiF₆²⁻ anions and the cyclen amino-groups contribute appreciably to the stability of the ternary complex. Thus, the present study provides a novel type of complementary SiF₆²⁻ recognition by the tetramine ligand with high selectivity in aqueous solution. [12]aneN₄ displays a great propensity to bridge SiF₆²⁻ anions, giving rise to a highly complicated structure.

References

1. M. Shionoya, E. Kimura, and M. Shiro: *J. Am. Chem. Soc.* **115**, 6730 (1993).
2. A.H. Krotz, L.Y. Kuo, and J.K. Barton: *Inorg. Chem.* **32**, 5963 (1993).
3. A. Bencini, A. Bianchi, E. Garcia-España, Y. Jeannin, M. Julve, V. Marcelino, and M. Philoche-Levisalles: *Inorg. Chem.* **29**, 963 (1990).
4. D.J. Hodgson, E. Pedersen, H. Toftlund, and C. Weiss: *Inorg. Chim. Acta* **120**, 177 (1986).
5. J.H. Reibenspies: *Acta Crystallogr.* **C48**, 1717 (1992).
6. J.H. Reibenspies and O.P. Anderson: *Acta Crystallogr.* **C46**, 163 (1990).
7. Yu.A. Simonov, Ed.V. Ganin, A.A. Dvorkin, M.S. Fonari, V.O. Gelmboldt, and A.A. Ennan: *Supramol. Chem.* **3**, 185 (1994).
8. V.O. Gelmboldt, Yu.A. Simonov, Ed.V. Ganin, M.S. Fonari, V.Ch. Kravtsov, A.A. Dvorkin, L.V. Ostapchuk, and A.A. Ennan: *Koord. Khim.* (Russ.) **22**, 21 (1996).
9. V.O. Gelmboldt, Ed.V. Ganin, L.V. Ostapchuk, A.A. Ennan, Yu.A. Simonov, J. Lipkowski, A.A. Dvorkin, and M.S. Fonari: *Zh. Neorg. Khim.* (Russ.) **41**(5), 1041 (1996).
10. G.M. Sheldrick: SHELXS-86. *Acta Crstallogr., Sect. A* **46**, 467 (1990).
11. G.M. Sheldrick: SHELXL-93. *Program for Crystal Structure Refinement*, Univ. Göttingen, Germany (1993).
12. M. Nardelli: *J. Appl. Crystallogr.* **28**, 659 (1995).
13. P. Thuéry, N. Keller, M. Lance, J.-D. Vigner, and M. Nierlich: *Acta Crystallogr.* **C51**, 1407 (1995).
14. T.N. Margulis and L.J. Zompa: *Acta Crystallogr.* **B37**, 1426 (1981).
15. J. Cullinane, R.I. Gelb, T.N. Margulis, and L.J. Zompa: *J. Am. Chem. Soc.* **104**, 3048 (1982).
16. Yu.A. Simonov, M.S. Fonari, J. Lipkowski, V.O. Gelmboldt, and Ed.V. Ganin: *J. Incl. Phenom.* **24**, 149 (1996).
17. M. Kojima, K. Nakabayashi, S. Ohba, S. Okumoto, Y. Saito, and J. Fujita: *Bull. Chem. Soc. Jpn* **59**, 277 (1986).
18. N. Matsumoto, A. Hirano, T. Hara, and A. Ohyoshi: *J. Chem. Soc. Dalton. Trans.* 2405 (1983).
19. J.H. Loehlin and E.B. Fleischer: *Acta Crystallogr.* **B32**, 3063 (1976).
20. B. Scott, K.J. Brewer, L.O. Spreer, C.A. Craig, J.W. Otvos, M. Calvin, and S. Taylor: *J. Coord. Chem.* **29**, 963 (1990).
21. J. Dale: *Isr. J. Chem.* **20**, 3 (1980).
22. J. Lipkowski: *Annual Reports on the Progress of Chemistry*, Royal Society of Chemistry, Vol. 92, Sect. C, p. 307 (1996).
23. D. Mootz, A. Albert, S. Schaeffgen, and D. Stäben: *J. Am. Chem. Soc.* **116**, 12045 (1994).
24. P.C. Manor and W. Saenger: *J. Am. Chem. Soc.* **96**, 3630 (1974).