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1-[*N*-(2-Aminoethyl)aminoalkyl]silatranes and their complexes with $CuCl_2$

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Abstract

1-[*N*-(2-aminoethyl)aminoalkyl]silatranes, $NH_2(CH_2)_2NH(CH_2)_n\overline{Si(OCH_2CH_2)_3N}$ (I, $n = 1$; III, $n = 3$) and their paramagnetic complexes with $CuCl_2$ (2 : 1) (III and IV) have been synthesized. Relevant ^1H and ^{13}C NMR data reveal, that the molecule I in the series of silatranes has the weakest transannular Si ← N bond. The pattern of the signals and the value of the *g*-factor in the ESR spectra of complexes III and IV in the crystalline state and in MeOH or DMSO solution points to distortion of the chelate planes and to conformational inhomogeneity. The fragmentation of complexes III and IV in Xe^0 fast atom bombardment (FAB) mass spectra indicates that the Si ← N bond in their molecules is stronger than those in the initial silatranes I and II.

1-Organylsilatranes bearing amino groups attached to the silicon atom in the organic radical have not been studied in any detail [1].

The 1-[*N*-(2-aminoethyl)aminoalkyl]silatranes (I, II) and their 2 : 1 coordinate compounds with $CuCl_2$ (III and IV) were prepared in order to investigate the effect of the nature of the aminoalkyl substituent on the strength of the coordinate Si ← N bond and to synthesize for the first time the novel, deep colored, paramagnetic metal-silatrane complexes.

$$H_2NCH_2CH_2NH(CH_2)_nSi(OEt)_3 \xrightarrow[-3\ HOEt]{+(HOCH_2CH_2)_3N}$$

$$H_2NCH_2CH_2NH(CH_2)_n\overline{Si(OCH_2CH_2)_3N} \xrightarrow{+CuCl_2}$$

(I, $n = 1$; II, $n = 3$)

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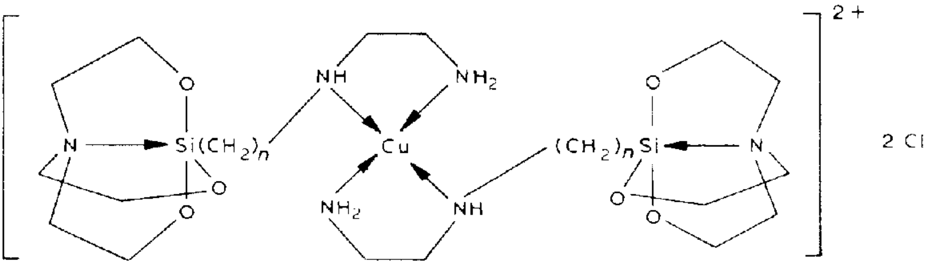


(III, $n = 1$; IV, $n = 3$)

The silatranes I and II are white crystalline substances, soluble in polar organic solvents. The yields, melting points and element analysis for these compounds are listed in Table 1.

Unlike the known 1-organylsilatranes bearing electron-accepting substituents in the methylene chain separated from the silicon atom by a $-(CH_2)_n-$ fragment, silatrane I ($n = 1$) shows a melting point significantly lower than that of its analogue II ($n = 3$).

In the ^1H NMR spectrum of silatrane I (in $CDCl_3$) the chemical shifts of endocyclic NCH_2 and OCH_2 groups are displaced to higher field, compared with those found for the known Si-substituted silatranes and for triethanolamine [3], whereas the chemical shifts in the spectra of silatrane II are nearly coincident with the corresponding chemical shifts of 1-chloropropylsilatrane (Table 2).

In the ^{13}C NMR spectrum of I (Table 2) the NC and OC resonance, of the silatrane ring carbon atoms, was also observed at higher field than that of the other silatranes studied [3].

The transannular bond length, $l_{Si \leftarrow N}$, in compound I calculated from the equation $\delta(NCH_2) = 5.46 - 21.21\, l_{Si \leftarrow N}$ ($r = 0.96$) [4] is within 2.40 ± 0.10 Å. This exceeds the known Si ← N bond lengths in silatranes with the exception of that in the platinum complex $(PhPMe_2)_2Pt(Cl)Si(OCH_2CH_2)_3N$ [5].

The complexes III and IV are fine-crystalline powders that are bright-blue and violet, respectively, are soluble in water, alcohols, dimethyl sulfoxide, and chloroform, and are paramagnetic. In the ESR spectrum of III in the crystalline state, anisotropy is less clearly evident than in the ethylenediamine complex (EDA-CuCl$_2$,

Table 1

1-[*N*-(2-Aminoethyl)aminoalkyl] silatranes $H_2NCH_2CH_2NH(CH_2)_n\overline{Si(OCH_2CH_2)_3N}$ (I, II) and their 2:1 complexes with $CuCl_2$ (III, IV)

Compound	*n*	Yield (%)	M.p. (°C)	Empirical formula	Anal. (Found (calc) (%))			
					C	H	N	Si
I	1	97.6	71–73	$C_9H_{21}N_3O_3Si$	43.59 (43.70)	8.68 (8.56)	16.76 (16.99)	10.80 (11.35)
II [a]	3	95.4	123–125	$C_{11}H_{25}N_3O_3Si$	–	–	–	–
III	1	87.3	168–173	$C_{18}H_{42}Cl_2N_6O_6CuSi_2$	34.86 (34.36)	7.04 (6.73)	13.18 (13.36)	
IV	3	66.1	192–195	$C_{22}H_{50}Cl_2N_6O_6CuSi_2$	38.01 (38.56)	7.49 (7.35)	11.96 (12.26)	

[a] M.p. 123–124°C, Ref. 2.

Table 2

^1H and ^{13}C chemical shifts in the NMR spectra of 1-[*N*-(2-aminoethyl)aminoalkyl]silatranes $NH_2CH_2CH_2NH(CH_2)_n\overline{Si(OCH_2CH_2)_3N}$ (I and II)

Compound	*n*	^1H, ^{13}C chemical shifts, δ, ppm, in $CDCl_3$				
		NCH_2	CH_2O	$SiCH_2$	$C-CH_2-C$	CH_2N
I	I	2.55(t)	3.47(t)	1.53(s)	–	2.27(m)
		49.8	56.3	40.0	–	40.2
II	3	2.73(t)	3.69(t)	0.32(m)	1.53(m)	–
		51.3	57.9	13.3	25.1	–

Table 3), and the band in the $g_{\parallel}$ region is broad and show no clear peak. For IV in which the silatranyl and ethylenediamine fragments are separated by a trimethylenic chain, the ESR spectrum is a single line (Fig. 1a, Table 3). On cooling the compounds III and IV to between −150 and −196 °C only increases the ESR signal intensity whereas the 2 EDA · $CuCl_2$ complex shows an enhanced $g_{\parallel}$ factor value.

Table 3

ESR spectral parameters for the complexes of $CuCl_2$ with ethylenediamine and *N*-(1-silatranylalkyl)ethylenediamines (III and IV)

Complex	Physical state	Temperature, (°C)	$g_{\parallel}$	$g_{\perp}$	g_c	a_{Cu}, *Oe*
2 EDA·$CuCl_2$	Powder	20	2.222	2.039	2.100	–
		−150	2.241	2.039	2.106	–
	In DMSO solution	20	–	–	2.120	80
		−150	2.194	2.031	2.085	191
	In MeOH solution	20	–	–	2.120	86
		−150	2.202	2.030	2.087	196
III	Powder	20	2.200	2.048	2.098	–
		−150	2.200	2.048	2.098	–
	In DMSO solution	20	–	–	2.080	–
		−150	2.202	2.040	2.098	185
	In MeOH solution	20	–	–	2.113	87
		−150	2.220	2.040	2.100	198
IV	Powder	20	–	–	2.092	–
		−150	–	–	2.092	–
	In DMSO solution	20	2.150	2.050	2.083	–
		−150	2.204	2.030	2.088	194
	In MeOH solution	20	–	–	2.131	80
		−150	2.223	2.040	2.101	179
$CuCl_2$	Powder	20	–	–	2.161	–
		−150	–	–	2.136	–
	In DMSO solution	20	–	–	2.161	–
		−150	–	–	2.136	–
	In MeOH solution	20	–	–	2.180	–
		−150	2.340	2.071	2.160	112

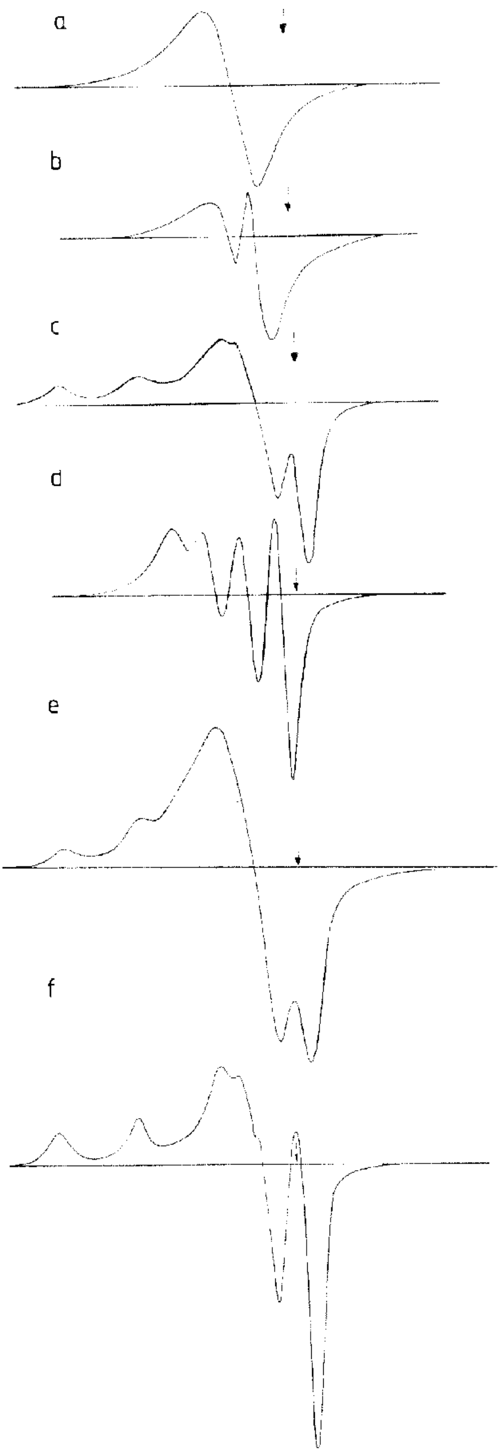


Fig. 1. ESR spectra of compounds III and IV (the position of the DPPH line is indicated by the arrow). (a) Powder (IV, 20 ° C); (b) Solution in DMSO (IV, 20 ° C); (c) Solution in DMSO (IV, −150 ° C); (d) Solution in MeOH (IV, 20 ° C); (e) Solution in MeOH (IV, −150 ° C); (f) Solution in MeOH (III, −150 ° C).

In the ESR spectra of crystals III and IV the averaging of not only hyperfine structure (HFS), but of the *g*-factor anisotropy is probably due to the disordered arrangement of chelate planes, especially pronounced in IV, in which the trimethylenic chain provides the greatest number of possible conformations.

The ESR spectra of methanolic solutions of III and IV (Fig. 1d) are isotropic and consist of four HFS components for the copper ion with a constant of ~ 85 *Oe*. This is consistent with a tetrahedrally distorted square-planar structure [6]. This structure, as a whole, remains intact in solution at low temperature. However, the change in the *g*-factor values (Table 3, Fig. 1e,f) indicates some secondary distortions of the square-planar structure of III and IV probably caused by bulky substituents, such as the silatranylalkyl groups.

At 20 °C the ESR spectrum of the complex IV in DMSO, consists of two components even when it is highly diluted (Fig. 1b), in contrast to that of 2 $EDA \cdot CuCl_2$ which shows an isotropic four-component signal. The ESR spectral parameters of anhydrous $CuCl_2$ in DMSO (Table 3) do not indicate any coordination of $CuCl_2$ to the solvent, hence there is no competition with the EDA-ligand in III and IV. Thus the observed nonhomogeneous broading of signals in the ESR spectra of complexes III and IV in DMSO solution is most likely to be a result of the reduced mobility of these bulky molecules in viscous solvent.

In the electron-impact mass spectra of I and II, the major peak corresponds to the silatrane skeleton ion $[M-R]^+$ (100%). Unlike the mass spectrum of silatrane II, the molecular ion $[M]^+$ (2.1%) is present in the mass spectrum of I. In addition to the loss of the substituent R, the mass spectra of I and II show a fragmentation pathway characteristic of silatranes with a weak, coordinate Si ← N bond, which involves an initial elimination of the silatrane skeleton OCH_2 group [7] (*m/e* 217 (20%) and 245 (25%), respectively).

Table 4

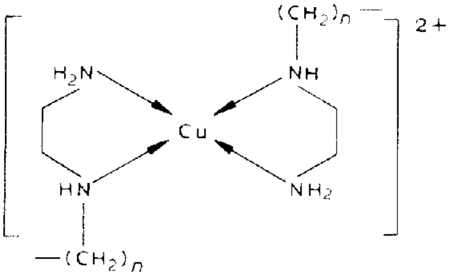
Principal ions in the Xe^0 Fast Atom Bombardment mass spectra of compounds I, III and IV [a]

Ion	*m/e* (intensity relative to the principle ion peak (%))		
	I	III ($M_2 \cdot CuCl_2$)	IV ($M_2 \cdot CuCl_2$)
$[M \cdot CuCl]^+$	–		375(7.7)
			373(9.7)
			348(4.4)
$[M \cdot Cu]^+$	–		340(9.9)
			338(22.7)
$[MH]^+$	248(62.0)	248(0.7)	276(24.3)
$[MH-NH_3]^+$	231(24.5)		
$[MH-OCH_3]^+$	217(20.4)	217(1.6)	245(5.2)
$[M-R]^+$	174(100)	174(100)	174(100)
$[TEA \cdot H]^+$	150(14.1)	150(1.7)	150(2.7)
	148(8.0)	148(4.6)	148(2.3)
	132(14.4)	132(15.8)	132(3.9)
$[M-R-OCH_2CH_2]^+$	130(13.8)	130(10.8)	130(6.2)
$[TEA-OCH_3]^+$	118(15.0)	118(5.2)	118(3.0)
		116(5.6)	

[a] Peaks of intensity over 1% and *m/e* 110 are presented. Among ions of lower intensity, the following ions were revealed: (compound, ion, *m/e*, %): III, $[MH]^+$, 248, 0.7; IV, $[HM_2 \cdot CuCl_2 - M]^+$, 411, 0.7.

For comparison the mass spectra of complexes III, IV and, I were recorded by use of Xe^0 fast atom bombardment (FAB). The principal ions are listed in Table 4.

The FAB spectrum of I shows an intense peak corresponding to the protonated molecular ion $[MH]^+$. An analogous ion appears after consecutive fragmentations of IV (m/e 276, 24%). At the same time, for III (the complex of two molecules of I with $CuCl_2$) the proportion of m/e 248 ion is less than 1% (Table 4). The silatrane skeleton ion $[M-R]^+$ (m/e 174, 100%) is the principal ion in the FAB mass spectra of I, III, and IV. An ion peak corresponding to a protonated TEA molecule (m/e 150, 14%) is observed for compound I. The appearance of the protonated ion of the initial trialkanolamine, $[HO(CH_2)_3NH(CH_2CH_2OH)_2]^+$ in the FAB mass spectra of the 1-organyl-3-homosilatranes, $\overline{Si(OCH_2CH_2)_2(OCH_2CH_2CH_2)N}$, detected in a cell containing glycerol, was attributed to their glycerolysis and/or hydrolysis [7]. In the spectra of III and IV the proportion of m/e 150 ions is less than 3% of the principal ion peak. That there is only a small proportion of these ions is indicative of the higher stability of III and IV to hydrolysis and glycerolysis as compared with that of I. The Si ← N bond is stronger in III and IV owing to the electron-accepting behaviour of the chelate substituents at the silicon atoms and to the bulkiness of these substituents, which prevents attack of hydroxyl-containing agent at the reaction center $Si(O)_3$. The increased proportion of silatrane skeleton ions $[N(CH_2CH_2O)_3Si]^+$ in the FAB spectra of III and IV as compared with that of I (11.1, 14.2 and 7.4%, respectively, of the full ion complement also provides evidence for a greater degree of Si ← N coordination in III and IV.



Experimental

^1H and ^{13}C NMR spectra were recorded with a JEOL FX-100 spectrometer (solvent $CDCl_3$, internal standard $Si(CH_3)_4$).

ESR spectra were recorded with a RE-1307 spectrometer in sealed, glass capillaries at temperatures between +20 and −196 °C. Side standards were DPPH and Mn^{2+} in MgO lattice. The concentrations of the compounds in the solutions were in the range: 10^{-1}–10^{-2} mol/l.

Electron-impact mass spectra were recorded with a JEOL JMS 0156-2 mass spectrometer.

Xe^0 FAB mass spectra were recorded with an IKB-2091 instrument equipped with a FAB-11 (Iontech. Ltd.) and connected to a PDP 11/34 computer. The bombardment of the sample was carried out with a Xe^0 atom beam, 7 keV, discharge current of 1 mA in a glycerol containing cell.

Toluene and diethyl ether were predried over sodium, and acetonitrile was predried over calcium hydride. All reagents were purified immediately before use.

N-[(2-Aminoethyl)aminomethyl]triethoxysilane. A mixture of 13.8 g (0.23 *M*) of ethylenediamine and 21.3 g (0.1 *M*) of (chloromethyl)triethoxysilane in 150 ml of dry toluene was heated at reflux for 8 h, then separated from the sediment by decantation. After removal of toluene the residue was distilled in vacuum. The yield of $H_2N(CH_2)_2NHCH_2Si(OC_2H_5)_3$ 7.2 g (30%), bp 110–111°C (1 mmHg), n_D^{20} 1.4296. Anal. Found: C 46.08, H 10.19, N 11.99, Si 12.49. $C_9H_{24}N_2O_3Si$. Calc.: C 45.73, H 10.23, N 11.85, Si 11.88%. ^1H NMR spectrum (δ, ppm, in $CDCl_3$): 1.09, s (NH); 1.23, t (CH_3C), 2.15, s (CH_2Si), 2.71, m (NCH_2–CH_2), 3.87, q (OCH_2).

1-[N-(2-Aminoethyl)aminoalkyl]silatranes, I and II. Triethanolamine (7.5 g, 0.05 *M*) was mixed with the corresponding *N*-[(2-aminoethyl)aminoalkyl]triethoxysilane $H_2N(CH_2)_2NH(CH_2)_nSi(OC_2H_5)_3$ where $n = 1$, 3 (0.05 *M*). Some minutes after the mixture had been homogenized the ethanol that formed was distilled off in vacuum. The yields, melting points and element analysis data of I and II are listed in Table 1.

Complexes III and IV were prepared by mixing the corresponding 1-[*N*-(2-aminoethyl)aminoalkyl]silatrane (I or II, respectively) in 10 ml of acetonitrile with a suspension of $CuCl_2$ (0.67 g, 0.005 *M*) in 15 ml of acetonitrile. The precipitate that formed was washed with diethyl ether and dried in vacuum. The yields, melting points and element analysis data are listed in Table 1.

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