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Synthesis and UV spectra of 8-mercaptoquinoline organosilicon derivatives and their metal halides complexes

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Abstract

IR and UV spectra of (8-quinolylthiomethyl)trimethylsilane (**1**), -trimethoxysilane (**2**), -silatrane (**3**) and their complexes with $CuCl_2$, $ZnCl_2$, $PtCl_2$ and $SnCl_4$ in MeCN have been studied. The UV spectra of 8-methylthioquinoline, its HN^+ cation and HN^+, HS^+ dication were calculated at the AM1 (CI) level. It was shown that **1**·$PtCl_2$, **2**·$ZnCl_2$ and **3**·$ZnCl_2$ are chelates. The **2**·$SnCl_4$ and **3**·$SnCl_4$ compounds have a strong N → Sn bond. The **2**·$CuCl_2$ and **3**·$CuCl_2$ complexes are a mixture of coordination compounds having N → Cu or N → Cu ← S bonds. © 2002 Elsevier Science B.V. All rights reserved.

Keywords: (8-Quinolylthiomethyl)trimethylsilane; (8-Quinolylthiomethyl)trimethoxysilane; 1-[8-(Quinolylthio)methyl]silatrane; Complexes; Metal chlorides; UV spectra

1. Introduction

8-Mercaptoquinoline forms coordination compounds with metal halides [1]. Up to now, the complexation of organosilicon *S*-derivatives of 8-mercaptoquinoline with metal chlorides has been studied only for K_2PtCl_4 [2]. The reaction of (8-quinolylthiomethyl)trimethylsilane with potassium platinum tetrachloride leads to a crystalline planar–square complex of five-membered chelate type L·$PtCl_2$.

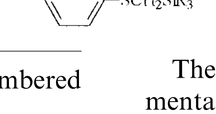
In this paper we report the synthesis and spectral properties of new coordination compounds of 8-mercaptoquinoline organosilicon derivatives and their metal complexes.

2. Results and discussion

2.1. Synthesis

1:1 Complexes were obtained by the reaction of compounds **1**, **2** and **3** with the metal chlorides and hydrogen chloride in chloroform according to the general scheme:

$$\underset{1\text{–}3}{L} + MCl_n \rightarrow \underset{4\text{-}12}{L\ \ MCl_n}$$



R = Me **1**, $MCl_n = PtCl_2$ (**4**);
R = OMe **2**, $MCl_n = CuCl_2$ (**5**), $ZnCl_2$ (**6**), $SnCl_4$ (**7**), HCl (**8**);
R = 1/3 $(OCH_2CH_2)_3N$ **3**, $MCl_n = CuCl_2$ (**9**), $ZnCl_2$ (**10**), $SnCl_4$ (**11**), HCl (**12**)

The physico-chemical characteristics and data of elemental analysis of compounds **4**–**12** are listed in Table 1.

The compounds **4**–**12** are high melting colored powders, insoluble in non-polar organic solvents, soluble in DMSO and DMF at room temperature and in MeCN on heating. With an equimolar amount of HCl in ether, 1-(8-quinolylthiomethyl)silatrane (**3**) forms a 1:1 hydrochloride **12**. With excess HCl, cleavage of an endocyclic Si–O bond occurs according to the following scheme:

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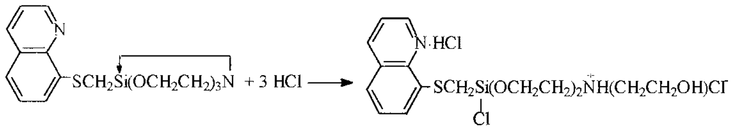

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The composition of product **13** is proved by the data of elemental analysis (Table 1). Broad band νOH (ca. 3300 cm^{-1}) and the silatrane skeletal vibration at 590 cm^{-1} in the IR spectrum is absent.

3. Spectroscopic studies

3.1. IR and UV–vis spectroscopy

The IR spectra of hydrochlorides **8**, **12** and of complexes **4**–**7**, **9**–**11** (KBr) were compared with those of the complexes of 8-mercaptoquinoline and its derivatives [1]. The spectra of compounds **1**–**3** are like the spectrum of 8-methylthioquinoline (**14**), but have some additional bands due to the presence of the organosilicon substituent CH_2SiR_3. These are, first of all, intense bands δ(Si–CH_3) at 870 and 1250 cm^{-1} for the ligand **1** and ν(Si–O) at 1080–1090 cm^{-1} for the ligand **2**. The IR spectra of hydrochlorides **8** and **12** were examined for the assessment of band displacement caused by protonation of only the nitrogen atom of ligands. The bands of quinoline bicycle stretching vibrations are most significantly changed in the spectra of **8** and **12** as with the hydrochloride of 8-methylthioquinoline [1]. The bands are displaced from 1490 to 1530 cm^{-1} and become considerably more intense, when the nitrogen atom protonated. The band at 980 cm^{-1}, simultaneously, which corresponds to γCH ring deformational vibrations, is shifted to the low-frequency region and its intensity is decreased.

The structure of the coordination compound of (8-quinolylthiomethyl)trimethylsilane with $PtCl_2$ (**4**), with N → Pt and S → Pt bonds are clearly identified by X-ray analysis [2]. The band at 1490 cm^{-1} corresponding to the ligand **1** is shifted to 1500 cm^{-1} in the IR spectrum of **4**. Despite some contribution of the ν(C–S) vibration to the ligand **1** band at 650 cm^{-1} [1,3], the S → Pt bond formation does not change its position. A high-frequency shift (by 8–10 cm^{-1}) of the quinoline group vibration band at 1490 cm^{-1} and its increase in intensity are also observed in the spectra of complexes **4**–**7**

Table 1
Complexes of $C_9H_6NSCH_2SiR_3$ **1**–**3** with MCl_n

N	R	MCl_n	Yield (%)	M.p. (°C)	Color	Brutto formula	Analysis (%) [a]					
							C	H	N	S	Si	Cl
4	Me	$PtCl_2$	62	204	Light-brown	$C_{13}H_{17}NCl_2SSiPt$	30.32 30.41	3.12 3.34	2.91 2.73	6.71 6.25	5.51 5.47	13.70 13.81
5	OMe	$CuCl_2$	96	165	Light-green	$C_{13}H_{17}NCl_2SSiCuO_3$	36.20 36.32	3.95 3.98	3.50 3.26	8.32 7.46	6.60 6.53	16.98 16.50
6	OMe	$ZnCl_2$	86	125	Pale-yellow	$C_{13}H_{17}NCl_2SSiZnO_3$	36.35 36.17	3.91 3.97	3.30 3.24	7.69 7.43	6.73 6.50	16.38 16.42
7	OMe	$SnCl_4$	78	178	Yellow	$C_{13}H_{17}NCl_4SSiSnO_3$	28.34 28.09	3.05 3.08	2.46 2.52	5.86 5.77	4.93 5.05	25.64 25.51
8	OMe	HCl	82	165	Bright-yellow	$C_{13}H_{18}NClSSiO_3$	46.94 47.05	5.18 5.47	4.51 4.22	9.78 9.66	8.52 8.46	10.85 10.68
9	1/3$(OCH_2CH_2)_3N$	$CuCl_2$	98	230 (dec.)	Light-green	$C_{16}H_{20}N_2Cl_2SSiCuO_3$	39.46 39.79	4.17 4.17	5.71 5.80	7.44 6.64	5.41 5.81	16.16 16.68
10	1/3$(OCH_2CH_2)_3N$	$ZnCl_2$	97	225	Pale-yellow	$C_{16}H_{20}N_2Cl_2SSiZnO_3$	39.79 39.64	4.48 4.16	5.18 5.78	6.47 6.61	6.12 5.79	14.51 14.62
11	1/3$(OCH_2CH_2)_3N$	$SnCl_4$	90	246 (dec.)	Yellow	$C_{16}H_{20}N_2Cl_4SSiSnO_3$	31.82 31.56	3.34 3.31	4.12 4.60	5.02 5.27	4.69 4.61	24.39 23.29
12	1/3$(OCH_2CH_2)_3N$	HCl	97	190	Yellow	$C_{16}H_{21}N_2ClSSiO_3$	48.95 49.92	5.66 5.50	6.97 7.28	8.11 8.33	7.52 7.29	9.79 9.21
13	1/3$(OCH_2CH_2)_3N$	3HCl	87	152	Bright-yellow	$C_{16}H_{23}N_2Cl_3SSiO_3$	41.94 41.97	5.54 5.06	5.71 6.12	5.63 7.00	6.90 6.13	22.90 23.23

[a] Analytical data given as found/calc. (%).

Table 2
UV spectra of solutions in MeCN of **1**–**3**, their complexes and HN$^{+\,a}$ cations, of 8-methylthioquinoline (**14**) and its cation HN$^+$, and the calculated (AM1 (CI)) descriptions of the electron transitions ($\pi \rightarrow \pi^*$, $\sigma \rightarrow \pi^*$) of **14**, its cation HN$^+$ and dication (HN$^+$, HS$^+$)

ν_{exp}, cm^{-1} (ε) ^{b}						1.03ν_{calc}, cm^{-1} (f)	Electron transition
(**1**)	(**2**)		(**3**)		(**14**) [5]	(**14**)	
29 500 (5900)	29 800 (6500)		28 500 (6200)		29 600	27 100 (0.173)	$\pi \rightarrow \pi^*$
						28 900 (0.028)	$\pi \rightarrow \pi^*$
39 500 (26 100)	39 700 (37 100)		38 800 (22 600)		39 100	37 600 (0.127)	$\pi \rightarrow \pi^*$
42 200 sh.	42 600 sh.		42 000 sh.			38 200 (0.003)	$\sigma_{CS} \rightarrow \pi^*$
						38 500 (0.082)	$\pi \rightarrow \pi^*$
						39 400 (0.211)	$\pi \rightarrow \pi^*$
(**1**) HN$^+$	(**2**) HN$^+$	(**2**) SnCl$_4$	(**3**) HN$^+$	(**3**) SnCl$_4$	(**14**) HN$^+$ [5]	(**14**) N$^+$H	
26 000 (2300)	27 000 (1800)	26 500 (1900)	25 000 (1600)	24 400 (800)	27 000	21 900 (0.001)	$\bar{n}_s \rightarrow \pi^*$
				28 900 (3200) ^{c}		28 600 (0.060)	$\pi \rightarrow \pi^*$
31 600 (4800)	31 700 (6300)	31 500 (9000)	31 500 (2900)	31 600 (4200)	31 700	30 200 (0.013)	$\pi \rightarrow \pi^*$
32 500 sh.	32 500 sh.	32 500 sh.	32 500 sh.	32 500 sh.		31 800 (0.005)	$\bar{n}_s \rightarrow \pi^{*\,d}$
37 700 (20 600)	38 000 (29 500)	38 000 (28 800)	37 300 (16 300)	36 500 (9100)		37 500 (0.250)	$\pi \rightarrow \pi^*$
41 200 (13 900)	42 600 (32 800)	41 300 (35 400)		38 800 (18 700) ^{c}		38 600 (0.115)	$\pi \rightarrow \pi^*$
		43 400 (39 000)	42 600 (19 000)	42 600 (22 700)		41 800 (0.090)	$\pi \rightarrow \pi^*$
(**1**) PtCl$_2$	(**2**) ZnCl$_2$		(**3**) ZnCl$_2$			(**14**) N$^+$H, S$^+$H	
29 000 (5800) ^{c}	29 800 (4300) ^{c}		28 900 (3000) ^{c}			30 600 (0.081)	$\pi \rightarrow \pi^*$
31 200 (6100)	31 400 (4600)		31 400 (4900)			31 600 (0.074)	$\pi \rightarrow \pi^*$
32 200 (5700)	32 200 (4000)		32 400 (4500)				$\pi \rightarrow \pi^*$
39 800 (19 000) ^{c}	40 000 (23 100) ^{c}		38 500 (8900) ^{c}			38 800 (0.283)	$\pi \rightarrow \pi^*$
42 600 (28 400)	42 100 (24 700)		41 800 (19 200)			39 800 (0.009)	$\pi \rightarrow \pi^*$
						43 900 (0.379)	

[a] Spectrum in MeCN on HCl addition.

[b] Extinction coefficients in the spectra of complexes were calculated without taking into account dissociation in the solution.

[c] The absorption band of the complex is overlapped by a absorption band summary ligand.

[d] The third $\bar{n}_s \rightarrow \pi^*$ transition is at 33 900 cm^{-1} ($f = 0.002$).

and **9**–**11**. Other spectra frequencies of complexes **4**–**7** and **9**–**11** with Cu, Zn, Pt and Sn chlorides are practically identical.

The effect of both the organosilicon substituents at the sulfur atom in 8-mercaptoquinoline molecule and the nature of metal on the structure of coordinate compounds **4**–**7** and **9**–**11** has been investigated by UV spectroscopy and semiempirical AM1 quantum chemical calculations of electron transition energies using formalism of the configuration interactions [4].

A change in the organosilicon substituent at the sulfur atom does not influence much on the absorption band position in the UV spectra of compounds **1**–**3**. At the same time, the nature of the metal exerts a significant effect on the UV spectra of complexes (Table 2). Therefore, quantum chemical calculation was performed for 8-methylthioquinoline (**14**) which models the ligands used as well as for its cation (HN$^+$) and dication (HN$^+$, HS$^+$) modeling complexes in which the coordination interaction involves a non-bonding electron pair of either nitrogen atom or nitrogen and sulfur atoms simultaneously.

The calculated values of energies and oscillator forces of electron transitions of neutral molecule **14** and their assignment to corresponding absorption bands in the UV spectra of ligands **1**–**3** are presented in Table 2 and Fig. 1. The reasonable consistency between the theoretical and experimental UV spectra of neutral molecules allows their unambiguous interpretation. The long-wave absorption band (ca. $\nu = 29\,300$ cm^{-1}) in the spectra of compounds **1**–**3** is caused by two $\pi \rightarrow \pi^*$ transitions of nearly the same energy. The highest intensity is displayed by the lowest energy transition. The next three $\pi \rightarrow \pi^*$electron transitions and one $\sigma_{CS} \rightarrow \pi^*$ transition, which appears between the energy levels of deep lying σ_{CS}-MO and LUMO (1), are responsible for the system of short wavelength absorption bands with approximately maximum at $\nu = 39\,000$ cm^{-1}. The nature of electron transitions and their order in energetic scale are presented in Scheme 1 and Fig. 1.

The correlation of MO of neutral and protonated molecule **14** presented in Scheme and the UV spectra of cations **1**–**3** allow the spectra of complexes to be divided into two major types.

1. Complexes having spectra similar to those of monocations.
2. Complexes with spectra reminding those of dications.

According to calculations, protonation of the nitrogen atom in molecule **14** leads to a ca. 1400 cm^{-1} shift of the low-energy $\pi \rightarrow \pi^*$ transitions towards higher frequencies, though their intensity ratios do not change much (Table 2). From the experimental data, in going to cations of compounds **1**–**3** the hypsochromic shift of the corresponding band is ca. 2500 cm^{-1} (Table 2, Fig. 1a, b). On protonation of the nitrogen atom of molecule **14** the global maximum of the absorption band of the short wavelength system is shifted towards lower frequencies (Figs. 1 and 2). The global maximum shift and a change in the absorption band contour are caused by not only the shift of corresponding $\pi \rightarrow \pi^*$ transitions, but also by their inversion on the energy scale accompanied by a sharp change in relative intensities. Under protonation the long wave electron transition changes its orbital nature due to an 87° internal rotation of methyl substituent about the Csp^2–S bond (for neutral molecule $\theta = 12°$). In this case, electron transition passes from the energy level of non-bonding electron pair which was involved in the interaction with the heterocycle π-system in the neutral molecule, and corresponds to mono-electron excitation HOMO → LUMO(1) (the MO correlation and electronic character of the most long wave band are presented in Scheme 1). This induces the appearance of an additional absorption band of cation (HN^+) of molecule **1** in the low-energy spectra region (Fig. 1b). Besides, the calculations indicate the presence of two more $\bar{n}_s \rightarrow \pi^*$ transitions in the spectrum. One of them, characterized by more intensity, is presented in Scheme 1 and Fig. 1. The corresponding excited state is conditioned by a multi-electron effect, but the great deal is contributed by a locally excited configuration $\bar{n}_s^1\pi^0\pi^1$. Due to its energy position (Fig. 1b) and low intensity, this transition is masked by the absorption band of $\pi \rightarrow \pi^*$ transitions. The presence of an additional long wavelength band (ca. 26 000 cm^{-1}) in the monocation **1** spectrum indicates the formation of a strong chemical bond involving non-bonding electron pair of the nitrogen atom. As the UV spectra of *S*-substituted 8-mercaptoquinoline **2**·$SnCl_4$ and **3**·$SnCl_4$ complexes are similar to the spectrum of cation **1** (HN^+) (Table 2, Fig. 1c), the com-

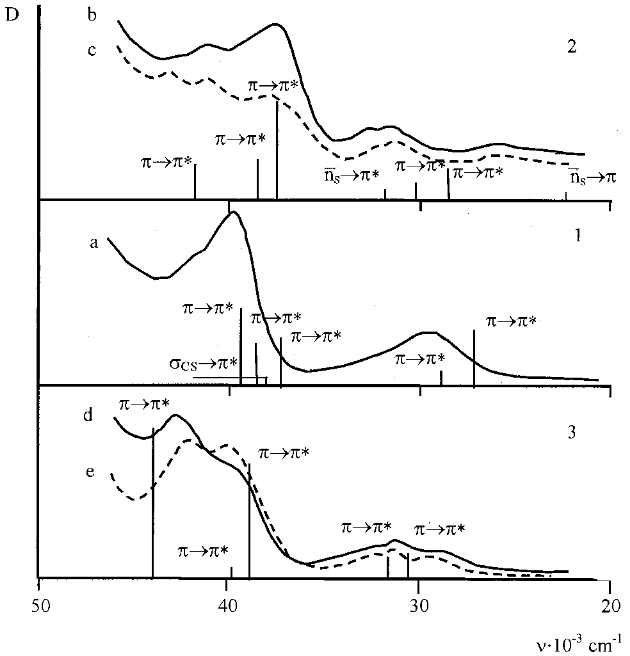
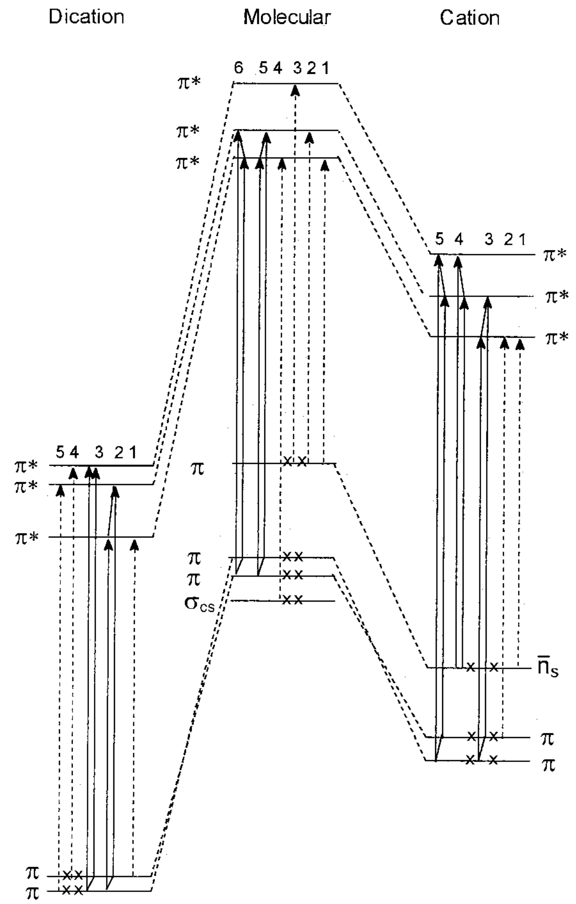


Fig. 1. UV spectra of solution in MeCN: (**1**) (a), cation (HN^+) of (**1**) (b), complexes **2**·$SnCl_4$ (**7**) (c), **1**·$PtCl_2$ (**4**) (d), **2**·$ZnCl_2$ (**6**) (e) and calculated energies of electron transfers represented by the vertical lines: (**14**) (1), cation (HN^+) of (**14**) (2), dication (HN^+, HS^+) of (**14**) (3).



Scheme 1. Solid double arrows design multiconfigurational transitions, dotted ones—one electron transitions.

plexes are suggested to have a strong, close to ionic N → Sn bond.

The calculated electron absorption spectrum of dication (HN^+, HS^+) of molecule **14** demonstrates an increase in the energy of $\pi \rightarrow \pi^*$electron transitions responsible for both short and long wavelength absorption bands. The long wavelength transition of type $\bar{n}_s \rightarrow \pi^*$ disappears in the dication spectrum as a result of the sulfur atom protonation. The energy arrangement and intensity ratio of dication electron transitions are in adequate agreement with the absorption band characteristics observed in the spectrum of the **1**·$PtCl_2$ complex (Fig. 1d) having a chelate structure according to X-ray diffraction [2].

Thus, owing to its spectral data, the dication of heterocycle **14** can serve as a model of a coordinative compound in which a metal atom simultaneously interacts with the nitrogen and sulfur atoms. In the case of the dication, the methyl substituent undergoes a 38° displacement from the quinoline cycle plane. Judging by UV spectra, an analogous type of interaction involving chelate formation is characteristic of the **2**·$ZnCl_2$ (Table 2, Fig. 1e) and **3**·$ZnCl_2$ complexes (Table 2). The absorption bands in the spectra of the **2**·$CuCl_2$ at 21 600, 25 000, 31 700, 32 500, 37 000, 38 700, 41 800 cm^{-1} (extinction coefficient is not determined for incomplete solubility of the complex) and **3**·$CuCl_2$ complexes [24 200 (2200), 31 400 (9600), 32 700 (10 300), 35 700 (11 200), 36 900 (11 700), 38 500 (12 000), 42 200 (31 900) cm^{-1}] are a mixture of coordination compounds having N → Cu or N → Cu ← S bonds (Fig. 2).

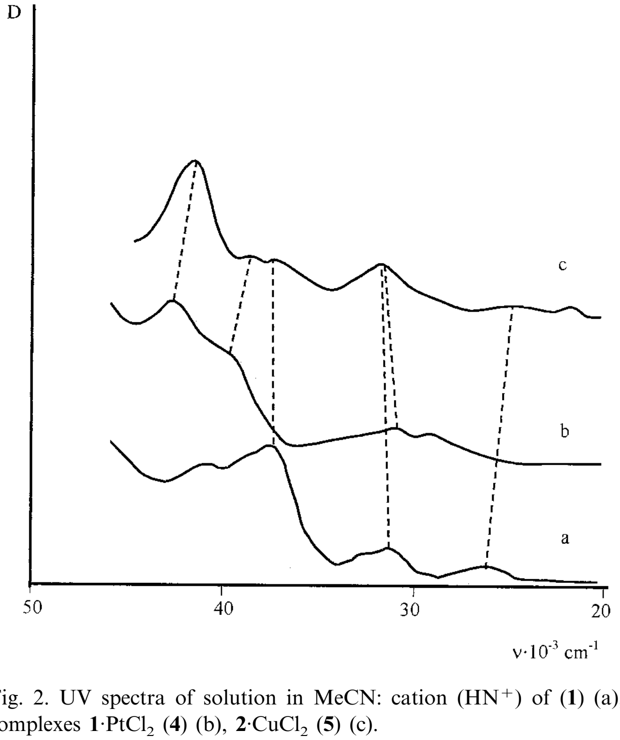


Fig. 2. UV spectra of solution in MeCN: cation (HN^+) of (**1**) (a), complexes **1**·$PtCl_2$ (**4**) (b), **2**·$CuCl_2$ (**5**) (c).

4. Conclusions

1. The experimental spectra of neutral molecules and cations having a protonated N atom differ greatly. Comparison of these spectra with those of the complexes of ligands **1–3** reveals some structural peculiarities of the complexes. Thus, the similarity between the spectrum of HN^+ cation **2** and **3** and the spectra of the corresponding **2(3)**·$SnCl_4$ complexes suggests the presence of a strong (evidently, ionic) N → Sn bond.
2. The chelate structure of the crystalline complex **1**·$PtCl_2$ (**4**) was retained in the solution. Analogously, in the **2(3)**·$ZnCl_2$ complexes the metal cation is coordinated to both heteroatoms (N and S). This is also supported by the similarity between their spectra and the theoretical spectrum of the HN^+, HS^+ dication.
3. The spectra of the **2(3)**·$CuCl_2$ complexes provide strong evidence that these complexes are present in MeCN solutions as an assembly of coordinate compounds of two types: one with the N → Cu bond and the other as a chelate with the N → Cu ← S bond.

5. Experimental

5.1. Preparation of complex of 1-[8-(quinolylthio)-methyl]silatrane and copper dichloride (9)

Compound **3** (2.14 g, 0.006 mol) in dry $CHCl_3$ (15 ml) was added to $CuCl_2$ (0.83 g, 0.006 mol) in dry $CHCl_3$ (15 ml). The reaction mixture was heated at 50 °C for 0.5 h. The precipitate was filtered off, washed with dry ether and dried under vacuum, to yield **9** (2.91 g, 98%), m.p. 230 °C (dec.).

Others complexes **5–8** and **10–12** were synthesized by a general procedure as described for **9** (Table 1).

5.2. General procedures and materials

IR spectra for compounds **1–14** as suspension in Vaseline oil or KBr pellets were obtained on a Specord 75 IR spectrometer. UV spectra of **1–14** in MeCN solution were recorded on a Specord UV–vis spectrophotometer. AM1 Quantum-chemical calculations of electron transition energies were performed in terms of configuration interaction (CI) formalism using the HYPERCHEM program [6]. In this case use was made of 200 lower-energy excited configurations appearing on electron excitation from six occupied onto six vacant MO.

Initial ligands **1–3** and complex **4** were synthesized according to [2,7].

Acknowledgements

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