ISSN 1070-3284, Russian Journal of Coordination Chemistry, 2009, Vol. 35, No. 4, pp. 312–316. © Pleiades Publishing, Ltd., 2009.
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A New Class of Electroluminescent Metal Complexes Based on Quinoline Ligands Containing the Sulfanylamino Group

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Received May 28, 2008

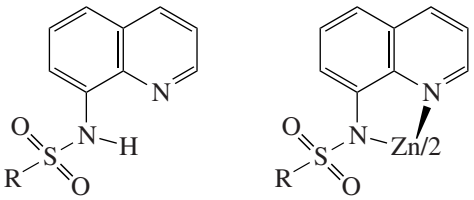
Abstract—The synthesis and properties of a new class of electroluminescent metal complexes based on quinoline ligands containing the sulfanylamino group in position 8 are described. These complexes contain C–N–M–N chains in the chelate cycles instead of the traditionally used C–O–M–N chains.

DOI: 10.1134/S1070328409040137

INTRODUCTION

Luminescent metal complexes based on organic ligands are of continuous interest in the recent years as electroluminescent materials for organic light-emitting diodes (OLED) [1–5]. Chelate metal complexes with ligands based on 8-hydroxyquinoline and its derivatives, for instance, well-known aluminum tris(8-hydroxyquinolate) and zinc bis(8-hydroxyquinolate), are often used as such materials [2, 3]. These and other presently known metal complexes used for OLED contain the chelate cycles including the C–O–M–N chains [2–6]. It seems of interest to study a possibility of replacing the oxygen atom in the chelate cycles by other heteroatoms, in particular, nitrogen atoms. The presence of bulky substituents at the nitrogen atoms can substantially affect the structure and properties of an electroluminescent material.

In the present article, we describe the synthesis and properties of the new class of electroluminescent metal complexes based on the quinoline ligands containing the sulfanylamino group in position 8



(L^1, L^2) (I, II)

L^1 and **I**: R = CH_3;
L^2 and **II**: R = 3,5-difluorophenyl (DFP)

In the sulfanylaminoquinoline derivatives, the hydrogen atom attached to the nitrogen atom is comparable in acidity to the corresponding hydrogen atom of the phenolic hydroxyl. This makes it possible to synthesize stable salts (metal complexes) with the zinc ion.

EXPERIMENTAL

The IR spectra of the ligands and complexes were recorded on Specord-75 and PerkinElmer Spectrum-BX instruments (KBr pellets). The ^{1}H NMR spectra were obtained in a dimethyl sulfoxide solution on a Bruker DRX 500 instrument with a working frequency of 500.13 MHz at 298 K using tetramethylsilane as the internal standard. Mass spectra were measured on a Finnigan MAT INCOS50 instrument with substance injection in the ionization area at an ionizing electron energy of 70 eV. The absorption spectra were measured for solids on a Specord M40 instrument by rubbing the substances on quartz. The photoluminescence spectra of the powders were measured on an Ocean Optics PC1000 instrument using excitation from a photodiode with an irradiation wavelength of 370 nm. The photoluminescence quantum yields of the powders were measured using a procedure described previously [4]. Aluminum tris(8-hydroxyquinolate) (AlQ_3) was used as the standard. Its photoluminescence quantum yield was 32% [7].

The L^1 and L^2 ligands were synthesized using a known procedure [8].

For L^1, ^{1}H NMR (δ, ppm): 3.15 (s, 3H, CH_3), 7.59–7.63 (dd. H^3), 7.64–7.68 (dd, H^6), 7.73–7.75 (d, H^7), 7.75–7.77 (d, H^5), 8.44–8.46 (d, H^4), 8.94–8.96 (d, H^2), 9.39 (s, NH); mass spectrum (m/z (I/I_{max}, %)): 222(43), 143(100), 116(75), 89(31), 63(22), 39(15).

For L^2, ^{1}H NMR (δ, ppm): 7.53–7.58 (m, 1H of Ph, H^3), 7.58–7.71 (dd, H^6), 7.63–7.70 (m, 2H of Ph), 7.69–7.72 (d, H^7), 7.73–7.76 (d, H^5), 8.38–8.40 (d, H^4), 8.85–8.87 (d, H^2), 10.5 (s, NH); mass spectrum (m/z (I/I_{max}, %)): 320(35), 256(40), 143(100), 116(78), 89(31), 63(27), 39(12).

Synthesis of zinc bis[(8-methanesulfanylamino)quinolinate] (I). A solution of sodium methoxide (prepared by the dissolution of sodium (0.23 g,

Table 1. Elemental analysis results and melting points of compounds L^1, L^2, **I**, and **II**

Compound	Empirical formula	Content (found/calculated), %					Mp, °C
		C	H	N	S	Zn	
L^1	$C_{10}H_{10}N_2O_2S$	55.74/54.04	4.78/4.54	12.15/12.60	14.34/14.34		146.5–147
L^2	$C_{15}H_{10}F_2N_2O_2S$	54.00/56.25	4.21/3.15	8.70/8.75	10.37/10.01		119–119.5
I	$C_{20}H_{18}N_4O_4S_2Zn$	47.57/47.30	3.99/3.57	10.36/11.03	11.46/12.63	12.86/12.87	>380
II	$C_{30}H_{18}F_4N_4O_4S_2Zn$	52.00/51.19	3.32/2.58	7.65/7.96	9.10/9.10		308–309

0.01 mol) in methanol (6 ml)) was added at room temperature to a suspension of ligand L^1 (2.22 g, 0.01 mol) in anhydrous methanol (25 ml). A precipitate of ligand L^1 sodium salt was formed. The mixture was stirred for 30 min, a solution of anhydrous zinc chloride (0.68 g, 0.005 mol) in anhydrous methanol (5 ml) was added dropwise, and the resulting mixture was stirred for 2 h on heating to 50–55°C. After cooling, a white precipitate was filtered off, washed successively with water and methanol, and dried in vacuo over P_2O_5. The yield of compound **I** was 2.41 g (95.1%). The substance was recrystallized from tetrahydrofuran. The product does not melt up to 380°C.

Synthesis of zinc bis[8-(3,5-difluorophenylsulfanylamino)quinolinate] (II). Ligand L^2 (1.92 g, 0.06 mol) was suspended in anhydrous methanol (25 ml), and a solution of sodium methoxide (prepared by the dissolution of sodium (0.14 g, 0.06 mol) in methanol (6 ml)) was added at room temperature. The resulting mixture was stirred for 30 min on heating to 35–40°C, and a solution of anhydrous zinc chloride (0.41 g, 0.003 mol) in methanol (10 ml) was added dropwise. A white precipitate was formed. The solution with the precipitate was stirred for 1 h at 35–40°C, cooled to room temperature, and the precipitate was filtered off, washed with water and methanol, and dried. The yield of compound **II** was 2.01 g (95%). The product was recrystallized from tetrahydrofuran.

The results of elemental analyses for ligands L^1 and L^2 and complexes **I** and **II** are given in Table 1.

RESULTS AND DISCUSSION

The structures of compounds L^1, L^2, **I**, and **II** were determined by elemental analysis and ^{1}H NMR, mass, and IR spectroscopy (Table 2). The mass spectra of ligands L^1 and L^2 exhibit lines corresponding to their molecular mass (222 and 320, respectively). Ligands L^1 and L^2 contain the N–H bond with the corresponding signals at 9.39 (L^1) and 10.5 (L^2) in the ^{1}H NMR spectra. The IR spectra of the ligands exhibit the absorption bands corresponding to the ν(N–H) vibrations at 3295 (L^1) and 3265 cm^{-1} (L^2). In complexes **I** and **II**, the nitrogen atom of the sulfanylamino group forms a coordination bond with the zinc atom, which is confirmed by the fact that the IR spectra of the complexes contain no absorption bands caused by the ν(N–H) vibrations.

The IR spectra of the ligands and complexes (Table 2) also exhibit absorption bands assigned to vibrations of the quinoline rings at 1600 and 1500 cm^{-1} characteristic of 8-hydroxyquinoline and its complexes with zinc and aluminum [9–13]. In addition, the bands characteristic of vibrations of the sulfo group at 1300–1400 and 1120–1190 cm^{-1} are observed [14–16].

The electronic absorption and photoluminescence spectra of the synthesized compounds in the visible spectral range are presented in the figure. The electronic absorption spectra of the ligands exhibit maxima at 242, 312 nm (L^1)) and 237, 283, 300, 320 nm (L^2). In the electronic absorption spectra of the complexes, the maxima are observed at 242, 265, 382 nm (**I**) and 265, 370 nm (**II**), and the longest-wavelength absorption band shifts substantially compared to that in the spectra of the corresponding ligands (from 320 to ~380 nm). The powders of complexes **I** and **II** possess intense photoluminescence with a maximum at 500 nm (**I**) and 465 nm (**II**). No appreciable photoluminescence was observed for ligands L^1 and L^2. The photoluminescence quantum yield of the powders of complexes **I** and **II** is 20 and 90%, respectively, which is comparable with or exceeds the quantum yield of the widely used electroluminescent material AlQ_3, being 32% [7, 17].

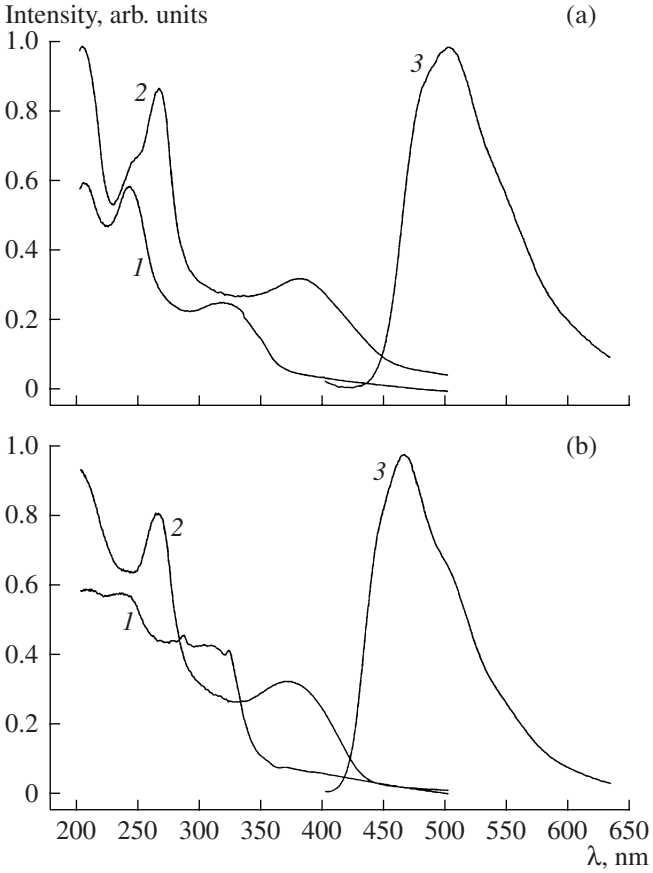
Owing to good luminescence properties, complexes **I** and **II** can be used as emitting materials in electroluminescence devices. As compared to traditionally used 8-hydroxyquinoline derivatives [2–5], they have several advantages: bulky substituents at the nitrogen atom should prevent the fast crystallization of the metal complexes during the operation of a device and also can shield the approach of a water molecule to the nitrogen–metal bond, thus impeding the hydrolysis of the metal complex. All these factors retard degradation properties and enhance the time source of the electroluminescence devices [2, 3].

Table 2. Vibration frequencies (ν, cm^{-1}) in the IR spectra of compounds L^1, L^2, **I**, and **II** and their assignment

Vibration frequencies (cm^{-1})				Assignment
L^1	**I**	L^2	**II**	
3295 vs		3265 vs		ν(NH)
	3100 w.sh	3100 w		
3060 w	3065 m.br	3070 w	3080 s	ν(CH) (quinoline)
3030 m	3020 s	3032 m	3045 m	ν(CH) (quinoline)
3015 m	3010 sh			ν(CH) (quinoline)
2935 s	2960 w.br			ν(CH) (CH_3)
2920 s	2930 s			ν(CH) (CH_3)
2850 m	2855 m			ν(CH) (CH_3)
1620 w	1602 w			ν(CC), δ(CCC)
		1605 vs	1605 vs	ν(CC), δ(CCC) (quin + DFP)
1595 w.sh		1595 w		
1580 m	1582 s	1587 m	1585 m	ν(NC), δ(CCH), δ(CCC)
1500 vs	1501 vs	1500 vs	1500 vs	ν(CC), δ(CCH), δ(CCC)
1470 s.br	1465 vs	1480 sh		
		1465 sh		
		1450 m.br	1467 s	ν(CC), δ(CCH), δ(CCC)
		1435 vs	1440 vs	(DFP)
				ν(CC), δ(CCH), δ(CCC)
				(DFP)
1430 w.sh	1430 w			$\delta_{as}(CH_3)$
1420 w.sh	1420 w			$\delta_{as}(CH_3)$
		1410 m		
1408 vs	1391 vs	1370 m	1390 s	$\nu_{as}(SO_2)$, ν(CN)
1380 w	1385 s	1335 vs	1380 s	$\nu_{as}(SO_2)$, ν(CN)
1375 w				$\delta_s(CH_3)$
1358 s	1330 vs	1310 m	1330 vs	$\nu_{as}(SO_2)$, ν(CN)
1330 s	1320 s	1298 vs	1290 vs	$\nu_{as}(SO_2)$, ν(CN)
1305 s	1282 vs.br		1270 sh	$\nu_{as}(SO_2)$, ν(CN)
1235 w	1267 w.sh	1247 w	1240 w	
	1245 w	1220 vw	1205 w	
	1205 w.sh			
1172 m	1195 s		1190 s	$\nu_s(SO_2)$, δ(CCH)
1149 vs	1127 vs.br	1165 vs.br	1140 vs.br	$\nu_s(SO_2)$, δ(CCH)
1090 s		1135 w	1130 vs.br	$\nu_s(SO_2)$, δ(CCH)
		1120 vs	1120 vs.br	$\nu_s(SO_2)$, δ(CCH)
1060 m	1075 w	1085 s	1082 m	γ(CCH)
1025 w	1040 w	1050 m	1045 vw	
995 vw	995 vw	1030 w	1040 vw	
970 vs	975 vs	980 vs	985 s	ν(NS,) ν(SC), δ(NSC)
925 s	954 m	968 w.sh	970 vs	ν(NS,) ν(SC), δ(NSC)
895 w	895 vw	923 m		
		900 m	890 m	δ(CCC), ρ(CC)
		870 s	870 sh	δ(CCC), ρ(CC)

Table 2. (Contd.)

Vibration frequencies (cm^{-1})				Assignment
L^1	**I**	L^2	**II**	
855 m.br	880 s	852 s	855 m	δ(CCC), ρ(CC)
830 vs	827 s	825 s	820 m	δ(CCC), ρ(CC)
795 s	788 vs	795 vs	790 m.br	δ(CCC), ρ(CC), ν(SC)
760 s	765 m	760 s	785 m.br	δ(CCC), ρ(CC), ν(SC)
748 m	750 m	745 s	745 m	δ(CCC), ρ(CC), ν(SC)
		730 vw		
		720 vw		
635 w	640 m	670 vs	675 m	ν(ZnN), δ(NZnN)
		652 vs	663 w	ν(ZnN), δ(NZnN)
		638 vs	632 w.sh	ν(ZnN), δ(NZnN)
		608 Ò	606 vs	ν(ZnN), δ(NZnN)
570 w	588 w	595 w	590 m	ν(ZnN), δ(NZnN)
545 vs	550 vs	570 m	570 sh	ν(ZnN), δ(NZnN)
	540 w	555 w.sh		
520 m	525 m	530 w	535 m	ν(ZnN), δ(NZnN)
510 vs	515 vs	500 sh	508 s	ν(ZnN), δ(NZnN)
465 w	440 w	490 m	500 vw.sh	
		450 m	460 w	



Electronic absorption spectra of the (*1*) ligands (a) L^1, (b) L^2 and (*2*) complexes (a) **I**, (b) **II**; (*3*) photoluminescence spectra of (a) **I** and (b) **II**.

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