Russian Journal of General Chemistry, Vol. 75, No. 3, 2005, pp. 417–419. Translated from Zhurnal Obshchei Khimii, Vol. 75, No. 3, 2005, pp. 453–455.

Complexes of 3-Thioformyl-1,2-dimethylindole with Metal Salts

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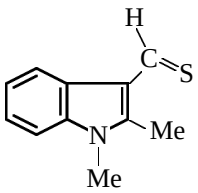
Received July 14, 2003

Abstract—3-Thioformyl-1,2-dimethylindole forms 1:2 molecular complexes with Co^{2+}, Ni^{2+}, and Zn^{2+} salts and 1:1 adducts with $CdCl_2$, $HgCl_2$, and $PbCl_2$. The IR spectra of these complexes indicate that 3-thioformyl-1,2-dimethylindole is coordinated to these metals via the sulfur atom of the thioaldehyde group.

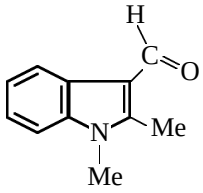
Synthesis of metal complexes with organosulfur ligands is an urgent problem of coordination and organometallic chemistry [1]. Thioaldehydes are insufficiently studied in this respect [2]. Previously we prepared 3-thioformylindole and its substituted derivatives [3]. The presence of the thiocarbonyl group in combination with a nitrogen-containing heterocycle makes these compounds unique complexing agents. Their metal complexes can exhibit specific biological activity.

We studied the reactions of Co^{2+}, Ni^{2+}, Zn^{2+}, Cd^{2+}, Hg^{2+}, and Pb^{2+} salts with the most stable thioformylindole derivative, 3-thioformyl-1,2-dimethylindole (L^1).

Cobalt(II) chloride, zinc(II) sulfate, and nickel(II) sulfate react with L^1 to form the molecular complexes $CoCl_2 \cdot 2L^1$ (**I**), $ZnCl_2 \cdot 2L^1$ (**II**), and $NiCl_2 \cdot 2L^1$ (**III**) (see table).



L^1



L^2

The IR spectrum of L^1 contains stretching and bending bands of the indole heterocycle with two methyl substituents in positions 1 and 2 (720, 1070, 1420, 1470, 1520, 1570, 1360, and 1480 cm^{-1}). The band at 965 cm^{-1} is assigned to the stretching vibrations of the thiocarbonyl group (cf. [4]).

In the IR spectra of complexes **I** and **II**, the resolved quartet of skeletal vibrations of the indole heterocycle (1400–1500 cm^{-1}) of free ligand L^1 dis-

Complexes of 3-thioformyl-1,2-dimethylindole (L^1) and 3-formyl-1,2-dimethylindole (L^2)

Comp. no.	Yield, %	mp, °C	Found, %					Formula	Calculated, %				
			C	H	Cl	N	S		C	H	Cl	N	S
I	74	218–220	51.16	4.24	14.67	5.51	12.63	$C_{22}H_{22}Cl_2CoN_2S_2$	51.97	4.33	13.97	5.51	12.60
II	90	198–200	50.81	4.65	13.79	5.36	13.25	$C_{22}H_{22}Cl_2N_2S_2Zn$	51.36	4.28	13.81	5.45	12.45
III	86	153–155	49.55	4.16	–	4.78	17.90	$C_{22}H_{22}N_2NiO_4S_3$	49.53	4.13	–	5.25	18.01
IV	69	140–141	55.56	5.29	13.40	5.47	–	$C_{25}H_{28}Cl_2CoN_2O_3$	56.18	5.24	13.30	5.24	–
V	84	150–152	65.16	5.15	–	6.87	15.56	$C_{44}H_{42}N_4NiS_4$	64.94	5.17	–	6.89	15.74
VI	72	>350	35.18	2.83	18.35	3.39	8.26	$C_{11}H_{11}CdCl_2NS$	35.48	2.96	19.09	3.76	8.60
VII	56	242 (decomp.)	28.32	2.39	14.73	3.08	6.36	$C_{11}H_{11}Cl_2NPbS$	28.27	2.36	15.20	3.00	6.85
VIII	50	>350	29.09	3.10	[a]	2.62	7.28	$C_{12}H_{15}Cl_2HgNOS$	29.21	3.04	14.40	2.84	6.49
IX	59	>350	24.95	2.54	26.07	2.14	–	$C_{11}H_{11}Cd_2Cl_4NO$	24.49	2.04	26.35	2.60	–

[a] Not determined.

1070-3632/05/7503-0417

appears, and a strong broad band is observed at 1490 cm^{-1}. The C–H bending vibrations of the benzene ring of L^1 at 740 cm^{-1} are also sensitive to complexation. In the spectra of complexes **I** and **II**, this band is observed at 750 and 759 cm^{-1}, respectively.

The IR spectrum of complex **III** contain bands of ligand L^1 and nickel sulfate. The sharp band of the free ligand is observed in the region from 1000 to 1200 cm^{-1}. The bands at 1068 and 1098 cm^{-1} are due to stretching vibrations of the S=O bond. The OSO bending band appears at 602 cm^{-1} [5].

In the spectra of complexes **I**–**III**, the band of C=S stretching vibrations is shifted to lower frequencies (940 cm^{-1}). These spectral transformations suggest coordination of 3-thioformyl-1,2-dimethylindole (L^1) via the sulfur atom of the thioformyl group [6]. In a DMSO solution these complexes decompose into the initial ligand L^1 and the corresponding metal salt, as judged from the ^1H NMR spectrum of the solution, containing the signal of the thioformyl proton of L^1 at 11.34 ppm (cf. [3]).

To refine the structure of complex **I**, we studied the reaction of $CoCl_2 \cdot 6H_2O$ with 1,2-dimethylindole and 3-formyl-1,2-dimethylindole (L^2) under the conditions of formation of complex **I**. No reaction between cobalt chloride and 1,2-dimethylindole was observed. In acetone, cobalt(II) chloride reacts with aldehyde L^2 to form the complex $CoCl_2 \cdot 2L^2 \cdot Me_2CO$ (**IV**). In the spectrum of this complex, the number of bands in the range 700–800 $cm^{-1}$is lower than that in the spectrum of free ligand L^2, and the intensities of the bands of the indole ring are redistributed. The low-frequency shift of the C=O stretching band from 1635 to 1600 cm^{-1} suggests coordination of L^2 via the carbonyl oxygen atom. The bands are 1630 and 1260 are due to incorporation of acetone molecules into complex **IV**.

Comparison of the IR spectra of complexes **I** and **IV** and those of ligands L^1 and L^2 shows that the electronic structure of the carbonyl ligand changes to lesser extent on the coordination than that of the thiocarbonyl ligand.

The reaction of nickel(II) acetate with 3-thioformyl-1,2-dimethylindole (L^1) yields $Ni(L^1)_2(L^1_{-H})_2$ (**V**). The ^1H NMR and IR spectra of this complex confirm the absence of acetate ion in the complex. It should be noted that L^2 does not react with nickel(II) acetate to form the similar complex.

The reaction of cadmium(II) and lead(II) chlorides with thioaldehyde L^1 in methanol yields molecular complexes $CdCl_2 \cdot L^1$ (**VI**) and $PbCl_2 \cdot L^1$ (**VII**), respectively. Mercury(II) chloride forms the complex $HgCl_2 \cdot L^1 \cdot MeOH$ (**VIII**).

As compared to the spectrum of free ligand L^1, a small hypsochromic shift of the bands of skeletal vibrations of the heterocyclic ring (1420–1510 cm^{-1}) is observed in the IR spectra of complexes **VI**–**VIII**. The number of these bands in the spectra of these complexes substantially decreases. The bands of bending vibrations of the aromatic protons are shifted to higher frequencies [from 740 to 756 (**VI**), 744 (**VII**), and 761 (**VIII**) cm^{-1}], and the C=S stretching bands, to the lower frequencies [from 965 to 939 (**VI**), 949 (**VII**), and 937 (**VIII**) cm^{-1}]. A strong band at 1093 cm^{-1} [ν(CO)] and a band at 1635 cm^{-1} [δ(OH)] [7] are present in the spectrum of complex **VIII** containing the methanol molecule.

Complex $CdCl_2 \cdot L^2$ (**IX**) was obtained by the reaction of cadmium(II) chloride with 3-formyl-1,2-dimethylindole (L^2). In the IR spectrum of this complex, the number of the bands of skeletal vibration of the heterocycle (1300–1600 cm^{-1}) decreases and the intensities of these bands are redistributed as compared to the spectrum of aldehyde L^2. The band of the carbonyl group is shifted from 1635 to 1613 cm^{-1}. The frequency of the C–H bending vibrations in the benzene ring (749 cm^{-1} for aldehyde L^2) remains virtually unchanged, whereas in the spectrum of complex **VI** this band is shifted by 17 cm^{-1}.

Comparison of the IR spectra of complexes **VI**–**VIII** and **I**–**III** with that of the free ligand L^1 shows that in all these complexes 3-thioformyl-1,2-dimethylindole is coordinated in the same manner.

EXPERIMNTAL

The IR spectra (KBr pellets) were recorded on Specord IR-75 and Bruker IFS-25 spectrometers. The ^1H NMR spectra were recorded in DMSO solution on a Jeol FX-90Q spectrometer at room temperature. HMDS was used as the internal reference. The reaction course was monitored by TLC on Silufol UV-254 plates using chloroform–ethyl acetate (2 : 1) as the eluent.

3-Thioformyl-1,2-dimethylindole (L^1) and 3-formyl-1,2-dimethylindole (L^2) were prepared by the procedures in [3] and [8], respectively.

The reactions of L^1 and L^2 with $CoCl_2 \cdot 6H_2O$ were performed in acetone, and the reaction with $NiSO_4 \cdot 7H_2O$, $Ni(CH_3COO)_2 \cdot 4H_2O$, $ZnCl_2$, $CdCl_2 \cdot 2.5H_2O$, $HgCl_2$, and $PbCl_2$, in methanol at the ligand-to-metal molar ratio of 2 : 1.

Complexes I–IX were prepared by stirring the cal-

culated amounts of organic ligand and metal salt in appropriate solvent at room temperature under an argon atmosphere. The reaction mixture was allowed to stand overnight at 5°C. The precipitate was filtered off, washed with acetone or methanol, and dried in a vacuum.

Complexes **I**, **IV** are green, **II**, **VI**–**VIII** yellow, and **III**, **V**, brown powders. The yields and some physicochemical properties of **I**–**IX** are presented in the table.

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