Available online at www.sciencedirect.com

ScienceDirect

Mendeleev Commun., 2018, **28**, 79–80

Mendeleev Communications

Synthesis and electrochemical study of 2-carbamoyl-4,5-dihydro-1,3,4-thiadiazole-containing ligands and their complexes with Cu^{II}, Co^{II} and Ni^{II}

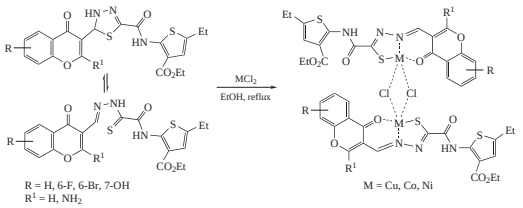
Ksenia A. Myannik,[a] Elena K. Beloglazkina,[b] Anna A. Moiseeva,[b] Tatiana K. Baryshnikova,[a] Vladimir N. Yarovenko[a] and Mikhail M. Krayushkin*[a]

[a] *N. D. Zelinsky Institute of Organic Chemistry, Russian Academy of Sciences, 119991 Moscow, Russian Federation. Fax: +7 499 135 5328; e-mail: mkray@ioc.ac.ru*

[b] *Department of Chemistry, M. V. Lomonosov Moscow State University, 119991 Moscow, Russian Federation*

DOI: 10.1016/j.mencom.2018.01.026

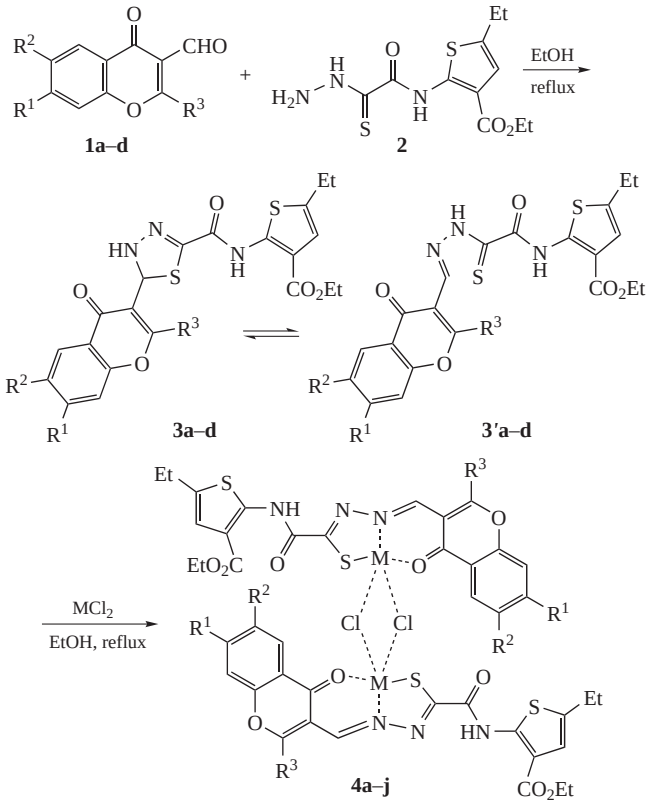
New organic ligands, 2-[*N*-(3-ethoxycarbonyl-5-ethylthiophen-2-yl)carbamoyl]-5-(4-oxo-4*H*-chromen-3-yl)-4,5-dihydro-1,2,4-thiadiazoles, and their complexes with Cu^{II}, Co^{II} and Ni^{II} chlorides, have been synthesized and examined by cyclic voltammetry.



Thiohydrazides of oxamic acids are of considerable interest in organic synthesis as polyfunctional organic substances that contain both electrophilic and nucleophilic atoms, and as bioactive compounds.[1] Based on them hydrazones possess biological activities and are considered as substrates for further construction of polycyclic aromatic structures.[2–5] Only a few examples of the complexing properties of such thiohydrazinyl-containing compounds have been reported,[6] therefore a study of oxamic acid thiohydrazones containing chromone moiety as novel ligands is perspective.

Here, we performed the reaction between 3-formylchromones **1a–d** and previously described thiohydrazide with thiophene moiety **2**[7] (the latter was successfully used in the synthesis of biologically active products[8]) affording dihydrothiadiazoles **3a–d** (Scheme 1). These compounds are formed in good yields by refluxing the reactants in ethanol; the products precipitate from the reaction mixture and do not require additional purification.[†] Coordination compounds **4a–j** were obtained by refluxing the solutions of the corresponding ligands and metal chlorides in ethanol.

In principle the obtained ligands can exist as two possible tautomeric forms, *viz.*, cyclic 4,5-dihydro-1,3,4-thiodiazole **3** and linear thiohydrazone **3′** ones (see Scheme 1). The ^{1}H NMR spectra (DMSO-d_6) of the ligands contain signals of the thiadiazoline protons at δ *ca.* 6.6 and 9.1 but no signal of NH proton of the hydrazone moiety. In the ^{13}C NMR spectra, signals of C^5 thiazoline atom are observed at δ *ca.* 61, while a signal of C=S



1, **3**	R^1	R^2	R^3	Yield of **3** (%)
a	H	H	H	49
b	OH	Br	H	74
c	H	H	NH_2	64
d	H	F	H	59

4	R^1	R^2	R^3	M	Yield of **4** (%)
a	H	H	H	Cu	60
b	H	H	H	Co	59
c	OH	Br	H	Cu	78
d	OH	Br	H	Co	76
e	H	H	NH_2	Cu	71
f	H	H	NH_2	Co	69
g	H	H	NH_2	Ni	58
h	H	F	H	Cu	59
i	H	F	H	Co	69
j	H	F	H	Ni	54

Scheme 1

† *Ligands* **3a–d** *(general procedure).* Formylchromone **1a–d** (1 mmol) was dissolved in a minimum amount of hot ethanol, and this solution was added to an equimolar amount of hydrazide **2** in ethanol (10 ml). The mixture was refluxed for 8 h and cooled to room temperature. The resulting precipitate was filtered off and dried in air. The spectral characteristics of the compounds obtained in this manner are given in Online Supplementary Materials.

Complexes **4a–j** *(general procedure).* An equimolar amount of a $MCl_2 \cdot 6H_2O$ salt (M = Co, Ni) or $CuCl_2$ in EtOH (1 ml) was added to a concentrated solution of ligand **3a–d** (0.05 g) in ethanol. The mixture was refluxed for 1 h and cooled to room temperature. The resulting precipitate was filtered off, washed with a small amount of diethyl ether and dried in air.

expected at δ 180–200 is missing. The structures of complexes **4a–j** were confirmed by IR and electronic spectroscopy. Previously,[9] we synthesized an analogous chromone-derived thioxamic acid hydrazone existing as a cyclic tautomer, which upon complexation with Cu^{II} turned into a linear form (X-ray data). Electronic and IR spectra of compounds **4a–j** are similar to those of the above complexes, which allows us to assume that they have similar binuclear structure with two hydrazone ligands and two bridging chlorine atoms. In the IR spectra of complexes **4a–j**, the absorption bands of C=O and N–N bonds are shifted. Also, a shift of C=N aldimine vibration bond by 5–10 cm^{-1} to shorter wavelengths in comparison with the free ligands indicates that the metal ion in the complex is coordinated by nitrogen atom. The C=S absorption band is missing in the IR spectra, which evidences that the ligand in **4a–j** exists as a thioenolic tautomer. Moreover, one of the N–H absorption bands disappears, which confirms this structure.

The electronic absorption spectra of complexes **4a–j** contain a high-intensity π–π* band of chromene ring transition at 260–270 nm (ε = 20000–36000 dm^3 mol^{-1} cm^{-1}).[10] Furthermore, in the spectra of Co^{2+} complexes two additional absorption bands are observed at 300 nm (ε ~ 30000 dm^3 mol^{-1} cm^{-1}) and 430 nm (ε ~ 17000 dm^3 mol^{-1} cm^{-1}). The spectra of Cu^{2+} complexes also contain two absorption bands at 350 nm (ε ~ ~ 21000 dm^3 mol^{-1} cm^{-1}) and 420 nm (ε ~ 29000 dm^3 mol^{-1} cm^{-1}). The spectra of Ni^{2+} complexes display a complicated picture at 260–400 nm, namely, a broad absorption band with five maxima. The described signals in the UV region can be assigned to various π–π* transitions in two conformation isomers with different spin states, as reported previously for nickel complexes of Schiff bases derived from 2-pyrazoline-5-thiones.[11] In the visible spectrum region, compounds **4a–f** manifest broadened peaks at 430–470 nm (ε ~ 21000 dm^3 mol^{-1} cm^{-1}) bathochromically shifted by ~50 nm in comparison with the free ligands, which can be assigned to the ligand–metal charge transfer (LMCT) in the complex molecule.[12]

To estimate the redox properties of the obtained compounds, ligands **3a–d** and their complexes **4a–j** were studied by cyclic voltammetry (CVA) on a glass carbon (GC) electrode in DMF solutions in the presence of 0.1 M Bu_4NClO_4 as the supporting electrolyte (for the voltammetry curves, see Online Supplementary Materials).

Quantum-chemical calculations of ligand molecules performed by PM3 semi-empirical method have shown that the HOMOs of the investigated molecules are mostly localized on the amidothiophene moieties, and the LUMOs are mostly localized on the carbamoylthiadiazoline ones (Figure 1). Based on this, it can be assumed that the initial oxidation of ligands **3a–d** should occur at the thiophene ring, whereas the reduction should occur at the carbonyl group and the thiadiazoline ring conjugated with it.

The reduction of studied ligands on a GC electrode occurs in three stages, except for compound **3c** whose reduction involves two stages. The reduction stages are irreversible, except for the phenol-containing ligand **3b**, where the second reduction peak is reverse. The oxidation of ligand molecules proceeds in two irreversible stages. The CVA curves of the copper-containing complexes contain two additional quasi-reversible one-electron peaks (see *e.g.*, refs. 13–17). The reverse scan of the voltammetric curves does not contain any peaks of oxidative desorption of metallic copper from the electrode surface, which indicates the stability of reduced forms of the complexes.[18] The cobalt-containing complex **4d** based on ligand **2b**, which bears OH and Br substituents in the chromone moiety, is apparently reduced reversibly at the ligand rather than at the metal. Presumably, nickel complex **4g** is reduced first at the metal and then at the ligand. The oxidation of all complexes occurs irreversibly in one or two stages, apparently at non-coordinated ligand moieties. Oxidation of coordinated chloride anions, whose reduction potential is usually *ca*. 1.2 V,[19,20] is also possible.

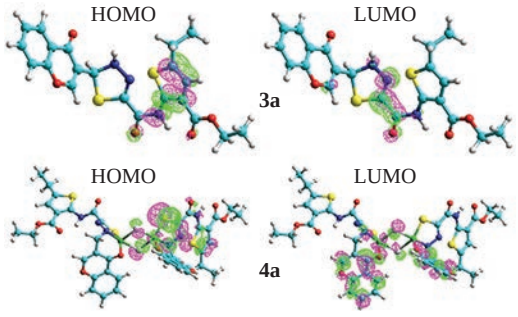


Figure 1 Frontier orbitals of ligand **3a** and its copper complex **4a**.

In summary, we synthesized a series of new organic ligands of chemotype **3**, and converted them into complex compounds with Cu^{II}, Co^{II} and Ni^{II} chlorides of type **4**. The compounds were characterized by spectral and electrochemical data.

This study was supported by the Russian Science Foundation (grant no. 14-50-00126).

Online Supplementary Materials

Supplementary data associated with this article can be found in the online version at doi: 10.1016/j.mencom.2018.01.026.

References

1 M. M. Abiev, V. Y. Butov, K. Y. Kurchenkov and E. Y. Khudainatov, *Patent WO 2010036148 A*, 2010.
2 A. V. Komkov, A. S. Komendantova, L. G. Menchikov, E. I. Chernoburova, Y. A. Volkova and I. V. Zavarzin, *Org. Lett*., 2015, **17**, 3734.
3 E. Dimitriadou, J. Stephanidou-Stephanatou, C. A. Tsoleridis, D. J. Hadjipavlou-Litina, C. Kontogiorgis and G. E. Kostakis, *Tetrahedron*, 2014, **70**, 2938.
4 V. P. Ananikov, K. I. Galkin, M. P. Egorov, A. M. Sakharov, S. G. Zlotin, E. A. Redina, V. I. Isaeva, L. M. Kustov, M. L. Gening and N. E. Nifantiev, *Mendeleev Commun*., 2016, **26**, 365.
5 K. A. Chudov, K. S. Levchenko V. A. Barachevskii, T. M. Valova, E. P. Grebennikov, P. S. Shmelin, N. O. Poroshin, G. E. Adamov, V. N. Yarovenko and M. M. Krayushkin, *Mendeleev Commun*., 2016, **26**, 521.
6 V. N. Yarovenko, A. V. Shirokov, P. A. Kondrashev, V. B. Rybakov, I. V. Zavarzin and M. M. Krayushkin, *Acta Crystallogr*., 2005, **E61**, m964.
7 A. V. Kamernitskii, E. I. Chernoburova, V. V. Chertkova, V. N. Yarovenko, I. V. Zavarzin and M. M. Krayushkin, *Russ. Chem. Bull., Int. Ed*., 2006, **55**, 2117 (*Izv. Akad. Nauk, Ser. Khim*., 2006, 2038).
8 A. L. Gintsburg, N. A. Zigangirova, E. S. Zayakin, M. M. Krayushkin and V. N. Yarovenko, *Patent RU 2447066*, 2012.
9 K. A. Myannik, V. N. Yarovenko, E. K. Beloglazkina, A. A. Moiseeva and M. M. Krayushkin, *Polyhedron*, 2018, **139**, 208.
10 D.-D. Qin, Z.-Y. Yang, T.-R. Li and G.-F. Qi, *Helv. Chim. Acta*, 2009, **92**, 525.
11 L. Hennig, R. Kirmse, O. Hammerich, S. Larsen, H. Frydendahl, H. Toftlund and J. Becher, *Inorg. Chim. Acta*, 1995, **234**, 67.
12 M. Atmeh, N. R. Russell and T. E. Keyes, *Polyhedron*, 2008, **27**, 1690.
13 D. B. Rorabacher, *Chem. Rev*., 2004, **104**, 651.
14 J. Liu, S. Chakraborty, P. Hosseinzadeh, Y. Yu, S. Tian, I. Petrik, A. Bhagi and Y. Lu, *Chem. Rev*., 2014, **114**, 4366.
15 C. Santini, M. Pellei, V. Gandin, M. Porchia, F. Tisato and C. Marzano, *Chem. Rev*., 2014, **114**, 815.
16 W. Kaim and J. Rall, *Angew. Chem. Int. Ed*., 1996, **35**, 43.
17 P. L. Boulas, M. Gómez-Kaifer and L. Echegoyen, *Angew. Chem. Int. Ed*., 1998, **37**, 216.
18 E. K. Beloglazkina, I. V. Yudin, A. G. Mazhuga, A. A. Moiseeva, S. V. Zatonskii and N. V. Zyk, *Russ. Chem. Bull., Int. Ed*., 2008, **57**, 577 (*Izv. Akad. Nauk, Ser. Khim*., 2008, 565).
19 A. G. Majouga, E. K. Beloglazkina, S. Z. Vatsadze, A. A. Moiseeva, K. P. Butin and N. V. Zyk, *Mendeleev Commun*., 2004, 115.
20 E. K. Beloglazkina, A. G Majouga, R. B. Romashkina, A. A. Moiseeva and N. V. Zyk, *Polyhedron*, 2007, **26**, 797.

Received: 2nd August 2017; Com. 17/5324