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Mendeleev Commun., 2018, **28**, 205–207

Mendeleev Communications

Synthesis and structure of nickel and copper chelate complexes with coumarin azo ligand

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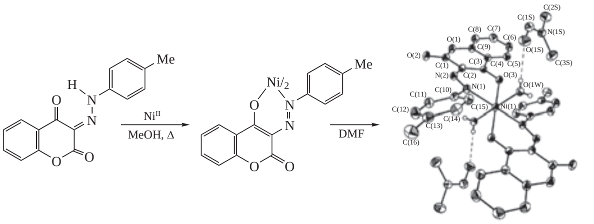
DOI: 10.1016/j.mencom.2018.03.033

Copper and nickel complexes with coumarin 3-azo derivatives were synthesized and characterized using IR and UV spectroscopy, magnetochemistry, quantum-chemical calculations and X-ray diffraction analysis. The data obtained on molecular and crystal structures of nickel metal chelate is the first instance in the series of metal complexes of coumarin 3-azo derivative.



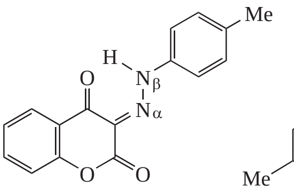
The azo compounds and their complexes find application as synthetic colorants[1] as well as components of new materials in medicine, catalysis, and other branches of science and technique.[2–6] Redox active azo ligands due to interaction with metal ions form the unusual reaction products and complexes with interesting magnetic and catalytic properties.[7–9] On the other hand, the permanent interest in natural and synthetic coumarin derivatives, including appropriate coordination compounds, is governed by a broad range of their biological, pharmacological, photochemical, and photophysical activities.[4,7,10–13] The presence of potential donor centers, oxygen atoms of coumarin fragment and two nitrogen atoms of the N=N group of arylazo moiety, and the ability to form five- and six-membered metallacycles make these compounds the promise models for studying competitive coordination and binding isomerism.[14] Based on azocoumarin metal chelates, the molecular switches[15] and the materials for optical recording[16] can be produced. In spite of numerous works on coordination compounds of coumarin, the complexes based on 2*H*-chromene-2,4(3*H*)-dione 3-azo derivatives[16–19] still remain not adequately explored.

The formation of five- and six-membered metal-chelate rings in the nickel(II) complexes, *E*/*Z* isomerization of the azo fragment[15] and the structural interconversions of square-planar and tetrahedral nickel(II) complexes[14,20] accompanied by the transition from diamagnetic (planar) to paramagnetic (tetrahedral) state make these compounds prospective for molecular electronics.

The aim of this work was the synthesis and investigation of structural and physico-chemical properties of novel copper(II) and nickel(II) complexes of coumarin 3-azo derivative. The experimental studies were combined with computational data to evaluate the possibility of structural interconversion between the square planar and tetrahedral geometries of the NiN_2O_2 core and re-coordination of the nitrogen atoms of the azo fragment of ligands with the formation of five-membered metallacycles in these complexes.

Metal chelates **2a** and **3** were synthesized by reaction of compound **1** with copper and nickel acetates[18,21] (**1** : salt molar ratio of 2 : 1).[†] The adduct **4** forms when compound **2a** is recrystallized from the DMF solution.

According to the elemental analysis, the composition of complexes **2a** and **3** corresponds to formula ML_2 [HL is 3-(*p*-tolylhydrazono)chromane-2,4-dione **1**]. In the IR spectra of metal chelates **2a** and **3**, the characteristic band shift of the ν(C=O) stretching vibrations was 19 and 47 cm^{-1}, respectively, into the low-frequency region as compared with the band of 1736 cm^{-1} in the spectrum of compound **1**. Characteristic bands of vibrations of a free ligand at 1616 and 1606 cm^{-1} that meet the vibrations of N=N group[4,18,19] are shifted by 10–13 cm^{-1} into long-wave



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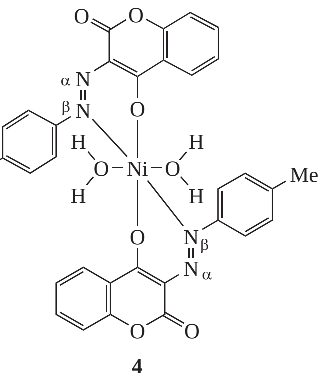

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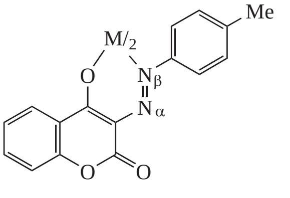


2a M = Ni
3 M = Cu

[†] *General procedure*. A solution of appropriate metal acetate (0.5 mmol) in methanol (5 ml) was added to a solution of hydrazone **1** (0.28 g, 1 mmol) in methanol (15 ml). Mixtures obtained were boiled for 2–3 h. Sediments settled were filtered, washed with methanol (3×5 ml) and dried.

region because of comlexation with metal ions. Note that the bands at 1500–1510 cm^{-1}, corresponding to the ν(C=C) vibrations of phenyl rings in the molecule of **1**,[4] are shifted multidirectionally upon the coordination of nickel and copper ions. The spectrum of nickel complex **2a** involves bands in low-frequency region ($\Delta\nu$ = ~10–14 cm^{-1}), while that of copper complex **3**, in high-frequency region ($\Delta\nu$ = ~5–14 cm^{-1}).

Being the product of crystallization of complex **2a** from DMF, adduct **4** is a paramagnetic substance (μ_{eff} = 2.81 μB), indicating its octahedral or tetrahedral configuration. The effective magnetic moment of copper compound **3** is 1.88 μB at room temperature and does not vary when temperature drops down to the boiling point of liquid nitrogen, being characteristic of the mononuclear molecular structure.

The structure of adduct **4** was corroborated by the XRD data,[‡] according to which it is crystallized in the form of the solvate with two DMF molecules (Figure 1). Unlike the square planar structure of metal chelate **2a**, in the case of compound **4**, the nickel ion within the center of inversion is coordinated with two water molecules occupying the axial positions. Thus, the coordinating center of metal chelate **4** has the centrosymmetrical trans-octahedral structure. The molecules of coumarin azo derivatives are monodeprotonated bidentate NO ligands bound with nickel ions by two oxygen atoms and two β-nitrogen atoms of N=N groups of both ligands. Two six-membered metallacycles formed by coumarin ligands have the 'sofa' conformation where the nickel atom deviates from the O(3)C(3)N(2)N(1) plane by 0.745 Å and has bending angle around O(3)–N(1) line of *ca*. 30°. The coumarin fragment is plane within ~0.04 Å.

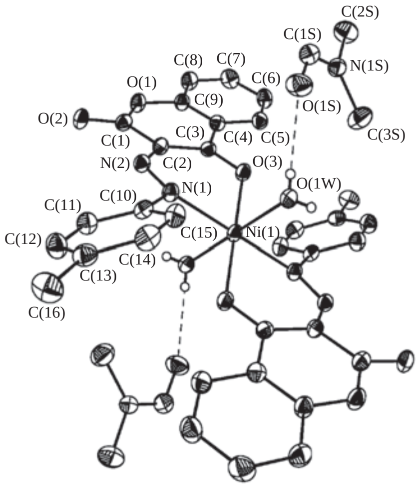


Figure 1 The structure of complex **4** in representation of atoms by thermal ellipsoids (p = 50%). The principal bond lengths (Å): Ni–O(3) 1.9889(16), Ni–N(1) 2.093(2), Ni(1)–O(1W) 2.1117(18), C(1)–O(2) 1.211(3), C(3)–O(3) 1.266(3), O(1)–C(1) 1.382(3), O(1)–C(9) 1.374(3), C(1)–C(2) 1.451(3), C(2)–C(3) 1.417(3), C(3)–C(4) 1.469(3), C(4)–C(9) 1.385(3), C(2)–N(2) 1.385(3), N(1)–N(2) 1.277(3), C(10)–N(1) 1.442(3).

Interatomic distances of heterocyclic fragment of coordinated coumarin azo ligand and metal ion and their distribution indicate the delocalization of ligand bonds. In comparison with hydrazone form of 1,3-[2-(5-*tert*-butyl-1,2-oxazol-3-yl)hydrazinylidene]chromane-2,4-dione,[22] the C(1)–O(2), C(3)–O(3), C(2)–N(2) distances in complex **4** become longer by 0.017, 0.034 and 0.067 Å, respectively, whereas the lengths of N(1)–N(2), C(1)–C(2), C(2)–C(3) bonds become shorter by 0.025, 0.022 and 0.043 Å, respectively. This testifies that ligands of adduct **4** are in azo form.

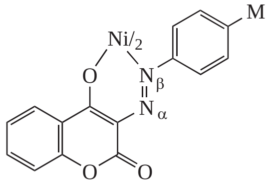
Inasmuch electron absorption spectrum (EAS) is one of the most important charactristics of the materials for creation of optical recording and molecular switches, we have studied their origin. The EAS of nickel and copper complexes **2a** and **3** in DMSO have the broad absorption band at 390 nm shifted by 40–43 nm to the short-wave region compared with that of the ligand. To interpret the EAS of compounds **1**–**4**, the quantum-chemical calculations were performed in the time-dependent density functional theory (TD-DFT) approximation using the B3LYP hybrid exchange-correlation functional,[23,24] the 6-31G(d) basis set[25] and the solvation model of polarizable medium (PMM) for DMSO solvent (for details, see Online Supplementary Materials).

According to the calculation data, the absorption band observed in EAS of compound **1** at 433 nm is mainly due to the HOMO → → LUMO electron transition (oscillator strength is 0.89) and has the character of the interligand charge transfer ^{1}ILCT.

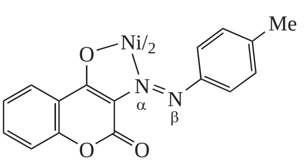
The long-wave maximum of the nickel complex **4** at 389 nm is determined by the group of electron transitions with relatively high values of oscillator strengths (> 0.1), the main contribution being due to transitions from HOMO-2,3,4 onto LUMO + 1. They are mainly characterized by metal–ligand charge transfer ^{1}MLCT, occurring from the MO that have high contributions of Ni 3*d* AO (up to 40%) onto LUMO + 1 where the whole electron density is practically localized on ligand atoms (~90%). Moreover, the electron transitions such as ligand–ligand charge transfer ^{1}LLCT contribute into the formation of this EAS band. Calculations also reveal the series of long-wave electron transitions (λ = 854.77, 755.9, 531.86 nm) with very small oscillator strengths (0.001–0.01), which occur from HOMO (73% 3*d* Ni) and HOMO-1 (40% 3*d* Ni) onto LUMO (100% L), which also have mainly ^{1}MLCT character.

Unlike metal chelate **4**, the EAS band at 393 nm in the spectrum of the copper complex **3** is due to electron transitions with high oscillator strength (0.77). In so far as 3*d* electron subsystem of copper ion is almost occupied as in both HOMO-1(α,β) and LUMO+1(β) and LUMO(α), the electron density is localized on the coumarin azo ligands, and the character of such transitions is determined as ^{1}LLCT.

Azo complexes with five-membered metallacycles are considered as the most promise objects to obtain molecular switches.[15] Switching process is based on reversible transition of *cis*-position of the complex azo fragment to *trans*-position. The possibility for re-coordination of metal atom of bis-chelates with different nitrogen atoms N$_\alpha$, N$_\beta$ (binding isomerism) can also be the starting point in creation of molecular switches. In this context, it is of interest to compare the relative energy parameters of nickel complexes with six- (**2a**) and five-membered (**2b**) metallacycles.



2a



2b

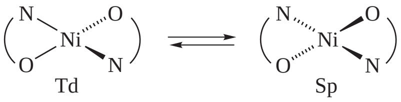
Compound **2a**: red-brown crystals, yield 73%, mp > 250 °C. UV-VIS [DMSO, λ/nm (ε)]: 390 (28950), μ_{eff} = 0 μB. Found (%): C, 62.17; H, 3.75; N, 8.95. Calc. for $C_{32}H_{22}N_4O_6Ni$ (%): C, 62.27; H, 3.59; N, 9.08.

Compound **3**: green powder, yield 82%, mp > 250 °C. UV-VIS [DMSO, λ/nm (ε)], 393 (30780), μ_{eff} = 1.88 μB at 297 K. Found (%): C, 61.65; H, 3.67; N, 8.89. Calc. for $C_{32}H_{22}N_4O_6Cu$ (%): C, 61.78; H, 3.57; N, 9.01.

[‡] *Crystal data for* $C_{32}H_{22}N_4O_6Ni\cdot 2[(CH_3)_2N]CHO\cdot 2H_2O$ **4**: crystals of $C_{38}H_{40}N_6O_{10}Ni$ (M = 799.47) are dark-green (0.25 × 0.2 × 0.2 mm), μ_{eff} = = 2.81 μB at 297 K, monoclinic, space group $P2_1/n$ at 120 K: a = 9.4163(5), b = 13.2659(8) and c = 14.7660(8) Å, β = 102.311(5)°, V = 1802.09(17) Å^3, Z = 2 (Z' = 0.5), d_{calc} = 1.473 g cm^{-3}. Intensities of 18 458 reflections were collected (2.09° < θ < 28.00°). The final refinement converged to wR_2 = = 0.1097 for all reflections [R_1 = 0.0505 was calculated for 3225 reflections with $I > 2\sigma(I)$], largest diff. peak/hole: 0.703/–0.388 e Å^{-3}.

CCDC 1556347 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre *via* http://www.ccdc.cam.ac.uk.

Ni^{II} complexes are expected to exhibit both configuration and spin isomerisms. They may form tetrahedral Td paramagnetic (high spin, triplet, $S = 1$) or square-planar Sp diamagnetic (low-spin, singlet, $S = 0$) complexes (Scheme 1).[14,20]



Scheme 1

The nickel complex **2a** is diamagnetic within a solid phase according to the magnetochemical data indicating the square planar structure of the coordination polyhedron. The result obtained agrees well with our data of quantum-chemical calculations by the DFT method using the B3LYP hybrid exchange correlation functional[23,24] and the TZVP basis set.[26] All the calculations were performed using the GAUSSIAN 03 program complex.[27] The molecular structures of **2a** have been fully optimized without any symmetrical constraint, at the level of the two singlet Sp and triplet Td cases. Calculations of molecule **2a** in gaseous phase have demonstrated that both tetrahedral and square planar structures are very close in energies, difference was only 0.48 kcal mol^{-1} indicating the possibility of the thermal configuration equilibrium of two forms in a solution. The result obtained testifies to the use of this system in molecular spintronics.

Quantum-chemical calculations (B3LYP/TZVP) of synthesized compound **2a** and modeling nickel metal chelate **2b**, where metal is coordinated with N_{α} atom of a ligand, show that the six-membered configuration (**2a**) is more favorable (by 14.9 kcal mol^{-1}) than five-membered one (**2b**). Such a difference in energy between **2a** and **2b** configurations indicates very small probability of the thermally excited transition between them. The change in the origin of donor atoms and substituents in the ligand system of such metal chelates quite possibly may result in the reverse binding isomerism of complexes under the action of external factors.

Thus, the nickel and copper complexes of coumarin azo aromatic ligand have been synthesized, and their spectral and magnetochemical parameters have been provided. According to the magnetochemical and X-ray diffraction data, the square-planar nickel complex **2a** is transformed into the octahedral metal chelate **4** under solvation conditions. The structure found for the latter is the first example in the series of metal complexes of coumarin 3-azo derivatives. According to the data of quantum-chemical calculations, both the tetrahedral and square-planar structures of nickel complex **2a** are very close in energy, and this fact indicates the possibility of thermal configuration equilibrium between two forms in a solution. The six-membered tetracoordinated configuration of nickel complex **2a** is more favorable in terms of energy than that of the five-membered one (**2b**).

The work was supported by the State Assignment in the Field of Scientific Activity of the Russian Federation (initiative research, project no. 4.6088.2017/8.9).

Online Supplementary Materials

Supplementary data associated with this article can be found in the online version at doi: 10.1016/j.mencom.2018.03.033.

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Received: 7th July 2017; Com. 17/5302