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Dedicated to Prof. Marian Mikołajczyk on the occasion of his 80th birthday

Novel copper(II), cobalt(II) and nickel(II) complexes with 5-(4-oxo-4H-chromen-3-yl)-4,5dihydro-1,3,4-thiadiazole-2-carboxamide: synthesis, structure, spectroscopic studies

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A series of novel organic ligands, 5-(4-oxo-4H-chromen-3-yl)-4,5-dihydro-1,3,4-thiadiazole-2carboxamide, which are the tautomeric forms of 2-oxo-2-(arylamino)-(2E)-2-[(4-hydroxy-2-oxo-2H-1-benzopyran-3-yl)-methyledene]ethanethioic acid hydrazides, have been synthesized from 3-formylchromone and oxamic acid thiohydrazides. Copper(II), cobalt(II) and nickel(II) with 2-oxo-2-(arylamino)-(2E)-2-[(4-hydroxy-2-oxo-2H-1-benzopyran-3complexes yl)methyledene]ethanethioic acid hydrazides have been synthesized by the interaction of corresponding organic ligands with MCl₂ (M=Cu, Co, Ni). The crystal structure of a copper(II) 5-(4-oxo-4H-chromen-3-yl)-N-phenyl-4,5-dihydro-1,3,4-thiadiazole-2complex with carboxamide has been solved by a single-crystal X-ray diffraction method. The copper(II) ions in complex molecule are coordinated by aldimine nitrogen atom, thiolate sulfur atom and the oxygen atom the pyrone ring keto-group as well as two bridged chloride anions in a distorted triangular bipyramidal geometry. The electrochemical investigations of synthesized ligands and complexes have been performed by cyclic voltammetry technique.

Key words: Chromones, 1,3,4-Thiadiazole, Oxamic acid thiohydrazide, Coordination compounds.

1. Introduction

Thiohydrazides of oxamic acids represent a wide synthetic interest as multifunctional organic compounds with both electrophilic and nucleophilic atoms, and possessing variety of biological properties [1,2]. Synthetic approaches basing on amide and thiohydrazide group of monothiooxamides modifications are promising for obtaining a wide range of diverse heterocyclic structure [3-6]. It is worth to note the tautomerism possibility of the product, leading

to the formation of 2, 3-dihydro- 1,3,4-thiadiazoIes or corresponding hydrazones, when thioaroylhydrazides are treated with aldehydes or ketones [7, 8].

Although, thiohydrazides are an interesting class of tridentate ligands because of their mixed hard–soft donor character and versatile coordination behavior. Only copper complex of salycilic aldehyde hydrazone and pyridine [9], and range of thiosemicarbazone complex [10], which can be considered as the analogs of the thiohydrazide oxamic acids were described previously.

The chromone (4H-benzopyran-4-one) skeleton is a fragment of the important flavone compounds, which occur naturally in plants and have potential beneficial effects for human health [11]. The metal complexes of chromone derived thiosemicarbazones exhibit antimicrobial [12], cytotoxic [13], antituberculostatic, anticancer, antioxidant [12] activities.

The hydrazone derived from the chromones are a perspective class of the organic compounds as due to their possible biological activity, as the ligand for metal ions complexation. In the present paper we report the synthesis and characterization of new 5-chromone-4,5-dihydro-1,3,4-thiadiazoles and also the study of these compounds as ligands in the reactions with copper(II), cobalt(II) and nickel(II) chloride.

2. Experimental

2.1. General

NMR spectra were recorded in deuterated solvents on spectrometers working at 300.13 MHz for 1H, 75.77 for 13C. Data are represented as follows: chemical shift, multiplicity (s, singlet; d, doublet; t, triplet; m, multiplet), coupling constant in hertz (Hz), integration, and assignment. Elemental analysis was performed on a Eurovector EA 3000 automated analyzer. Mass spectra were obtained on a mass spectrometer (70 eV) with direct sample injection into the ion source. Highresolution mass spectra were obtained from a TOF mass spectrometer with an ESI source. All chemicals and anhydrous solvents were purchased from commercial sources and used without further purification. Silica column chromatography was performed using silica gel 60 (70–230 mesh); TLC analysis was conducted on silica gel 60 F254 plates. UV–vis spectra were recorded in 1.0 cm quartz cuvettes. The experimental measurements were performed in the presence of air in DMSO solutions. IR spectra were registered on a Bruker ALPHA spectrometer in KBr pellets.

Electrochemical studies were carried out on a PI-50-1.1 potentiostat. Glassy-carbon disk (2 mm in diameter) was used as the working electrodes; a 0.05 M Bu4NClO4 solution in DMF served as the supporting electrolyte; Ag/AgCl/KCl(sat.) was used as the reference electrode. All measurements were carried out under argon; the samples were dissolved in the pre-deaerated

solvent. Dimethylformamide (high-purity grade) was purified by successive refluxing and vacuum distillation over anhydrous $CuSO_4$ and P_2O_5 . PM3 calculation were performed by use the HYPERCHEM software on PC. Geometry optimization of the molecules was carried out with a gradient less than 0.01 kcal/mol as the convergence criterion.

X-ray diffraction: single crystals of **7a** were obtained by the slow diffusion of diethyl ether to ethanolic solution of CuCl₂ and ligand **6a** (1:1). Single crystal data for **7a** were collected on a Bruker APEX2 DUO diffractometer using graphite monochromated Mo K α radiation ($\lambda = 0.71073$ Å) at 120 K. The structure was solved by direct method and refined by the full-matrix least-squares against F² in anisotropic approximation for non-hydrogen atoms. Hydrogen atoms were placed geometrically and refined in isotropic approximation in riding model. Crystals are monoclinic, space group C2/c, at 120 K: a = 14.8541(10) Å, b = 7.7072(5) Å, c = 29.621(2) Å, $\alpha = 90^{\circ}$, $\beta = 91.9116(13)^{\circ}$, $\gamma = 90^{\circ}$, V = 3389.2 (4) Å ³, Z=4, D calc = 1.761 Mg/m³, μ (MoK α) = 1.596 mm⁻¹, F(000) = 1816. CCDC 1575758 contain the supplementary crystallographic data, which can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccde.cam.ac.uk/data_request/cif.

2.2. 5-(4-oxo-4H-chromen-3-yl)-4,5-dihydro-1,3,4-thiadiazole-2-carboxamide 6–18 (typical procedure)

Compounds **1a-e** [14-17], **2a-e** and **3a-e** [18-19] were synthesized according to literature procedures. Solution of compounds **3** (1 mmol) in minimal amount of hot EtOH was added to an equimolar amount of **5** in 10 ml of EtOH. The mixture was boiled for 8 h, and then the precipitate was filtered, dried and recrystallized from EtOH. Spectral and HRMS data for **6a-o** are shown in Supplementary Materials.

2.3. Synthesis of coordination compounds 7a-z (typical procedure)

Concentrated solutions of ligand **6a-d**, **g-m** (0.05 g) in 5 ml of EtOH and equimolar amount of MCl_2*6H_2O (M = Co, Ni) or CuCl_2 in 1–2 ml of EtOH were mixed at room temperature, boiled for 1 h and stand to the complex precipitation. The forming solid was filtered off, washed by small portions of Et₂O and dried in air. Spectral and Elemental analysis data for **7a-z** are shown in Supplementary Materials.

3. Results and discussion

3.1. Synthesis of ligand and complexes

Hydrazones **6** were synthesized by the condensation reactions of 3-formylchromones **5**, obtaining by the Vilsmeier–Haack reaction from various 2-hydroxyacetophenones **4**, and previously described oxamic acid thiohydrazides **3** [18-19] (Scheme 1).



6a, R = Ph, $R_1 = H$, $R_2 = H$ (69%); **6b**, R = 4-F-C₆H₄, $R_2 = H$, $R_1 = H$ (60%); **6c**, R = Ph, $R_1 = H$, $R_2 = OH$ (70%); **6d**, R = Ph, $R_1 = Br$, $R_2 = OH$ (70%); **6e**, R = 4-F-C₆H₄, $R_1 = H$, $R_2 = OH$ (65%); **6f**, R = 4-F-C₆H₄, $R_2 = OH$, $R_1 = Br$ (66%); **6g**, R = Ph, $R_2 = H$, $R_1 = F$ (52%); **6h**, R = 4-F-C₆H₄, $R_2 = H$, $R_1 = F$ (40%); **6i**, R = 4-OMe-C₆H₄, $R_2 = OH$, $R_1 = H$ (55%); **6j**, R = 4-OMe-C₆H₄, $R_2 = OH$, $R_1 = Br$ (62%); **6k**, R = 4-OMe-C₆H₄, $R_2 = H$, $R_1 = F$ (49%); **6l**, R = 4-OMe-C₆H₄, $R_2 = H$, $R_1 = H$ (46%); **6m**, R = 2,5-(OMe)₂-C₆H₃, $R_2 = H$, $R_1 = H$ (49%); **6n**, R = 2,5-(OMe)₂-C₆H₃, $R_2 = H$, $R_1 = F$ (60%); **6o**, R = 3,5-Cl₂-C₆H₃, $R_1 = H$, $R_2 = H$ (69%);

Scheme 1. Synthesis of ligands 6a–o.

Note, that all of the compounds **6** basing on ¹H and ¹³C NMR data exist in DMSO solution as unexpected cyclic tautomeric form of *4H*-chromen-3-yl-4,5-dihydro-1,3,4-thiadiazole-4-carboxamides **6a-o**. Our earlier salicylic aldehyde thiohydrazone study showed that there are equilibrium mixture of two tautomers, linear A and cyclic B in solutions (Scheme 2) [15]. Instead of the hydrazinyl proton, the thiadiazole singlet is observed at 6.5 ppm, which indicates the presence of an intermolecular hydrogen bond (between HC-N proton and pyrone keto-group). ¹³C NMR spectra exhibit signal C₁₀ at 55-70 ppm and absence C=S in the range 180-200 ppm. Thus, it can be assumed that the equilibrium is shifted toward a cyclic form **B** for

compounds **6a-o** in the solution. *Trans*-configuration of ligand linear form **6a** was confirmed by the X-ray data for its copper complex **7a** (see below).

IR spectra of all synthesized ligands display absorption bands of C=O fragments in the 1650- 1700 cm⁻¹ region, C=N and C-N in 1500–1660 cm⁻¹ region of, N-N in 1020-1090cm⁻¹ region. Normally the "pure" C=S stretching frequency would observed in the 1080-1230 cm⁻¹ range [16] in our case it doesn't. Also this is an evidence of the cyclic form **B** existence in the solid state.



Scheme 2. Tautomeric equilibrium of thiohydrazones A and thiadiazoles B.

To obtain the coordination compounds, the solutions of ligands **6a-d**, **g-n** in ethanol were mixed with equimolar amount of CuCl₂ or CoCl₂*6H₂O, or NiCl₂*6H₂O ethanolic solution, the resulting mixture was reflux for 1 hour and than were standing to the solid precipitation. Complexes **7a-z** (Scheme 3) with (L-H)₂M₂Cl₂ composition (M = Cu, Co, Ni) were obtained in all cases («L» is the collective designation for organic ligands **6a-d**, **g-n**). All complexes are reasonably soluble in DMF or DMSO and stable in the atmospheric conditions for extended period.



Scheme 3. Synthesis of coordination compounds 7a-z.

Organic ligands fragments in complexes 7 are in linear form A, which can be determined on the basis of the significant shift of N-N bond absorption to the characteristic hydrazide 4 vibrations frequencies in the IR spectra of complexes. IR spectra of complexes 7a-z show also the shift of C=N group absorption bands at 1620-1600 cm⁻¹ compare to initial ligands which

confirms the metal ions coordination with the C=N nitrogen atoms. Also the vibration bands of C=O bonds are shifted as a result of complexation. The absorption band of C=S group doesn't appear in the IR spectra of complexes.

The electronic absorption spectra of complexes show high-intensive chromene cycle π - π^* [17] transition bands in the range 260-270 nm ($\varepsilon = 30000-5600 \text{ 1 mol}^{-1} \text{ cm}^{-1}$). The cobalt, copper and nickel complex show three additional absorbtion bands in UV-vis spectra around 300 nm ($\varepsilon = 20000-36000 \text{ 1 mol}^{-1}\text{ cm}^{-1}$), 340 nm ($\varepsilon = 28000-48000 \text{ 1 mol}^{-1}\text{ cm}^{-1}$) and 430 nm ($\varepsilon = 10000-20000 \text{ 1 mol}^{-1}\text{ cm}^{-1}$) or two, a wide band around 300 nm ($\varepsilon = 10000-30000 \text{ 1 mol}^{-1}\text{ cm}^{-1}$) and 450 nm ($\varepsilon = 10000-16000 \text{ 1 mol}^{-1}\text{ cm}^{-1}$). These bands refer to π - π^* transitions in the ligand molecules [18]. The bands in the visible region are observed at 430-470 nm for all coordination compounds. It is assigned 10-20 nm bathochromic shift for them comparing with ligand, what can be ligand-to-metal charge-transfer transitions.

The ligands **6j-m**, having the OMe substituent in the arylamide fragment, show a low intensive n- π transition at 450 nm. Ligand **6j** display a wide band 250-390 nm with two shoulders and peak at 304 nm ($\epsilon = 10600 \text{ 1 mol}^{-1}\text{cm}^{-1}$). Its complexes have in their UV-vis spectra the overlapping absorption bands around 260 nm ($\epsilon = 60000 \text{ 1 mol}^{-1}\text{cm}^{-1}$), 300 nm ($\epsilon = 58000 \text{ 1 mol}^{-1}\text{cm}^{-1}$) and 440 nm ($\epsilon = 20000 \text{ 1 mol}^{-1}\text{cm}^{-1}$.

3.2. Molecular and crystal structure of complex 7a



Figure 1. Molecular structure of complex 7a.

Table 1. Bond lengths [Å] and angles [°] for 7a

Bond lengths	d (Å)	Bond angles	ω(°)	Bond angles	ω(°)
Cu(1)-O(2)	1.968(2)	O(2)-Cu(1)-N(1)	90.14(8)	O(2)-Cu(1)-Cl(1)#1	87.10(6)
Cu(1)-N(1)	2.008(2)	O(2)-Cu(1)-S(1)	175.14(6)	N(1)-Cu(1)-Cl(1)#1	114.81(7)

Cu(1)-S(1)	2.2321(8)	N(1)-Cu(1)-S(1)	85.32(7)	S(1)-Cu(1)-Cl(1)#1	96.37(3)
Cu(1)-Cl(1)	2.3305(7)	O(2)-Cu(1)-Cl(1)	90.70(6)	Cl(1)-Cu(1)-Cl(1)#1	89.62(3)
Cu(1)-Cl(1)#1	2.6500(8)	N(1)-Cu(1)-Cl(1)	155.56(7)	Cu(1)-Cl(1)-Cu(1)#1	90.38(3)
Cl(1)-Cu(1)#1	2.6500(7)	S(1)-Cu(1)-Cl(1)	92.72(3)	C(10)-N(1)-N(2)	113.2(2)

The structure of complex 7a was established by X-ray diffraction. Crystallographic data and refinement parameters for 7a are shown in Supplementary Materials; selected bond lengths are given in Table 1. Molecular structure of compound 7a together with the atom-numbering scheme is shown in Fig. 1. The crystals, available for structural investigation, were made by slow diffusion of diethyl ether to ethanolic solution of CuCl₂ and ligand 6a (1:1).

The coordination compound is symmetrical relative to the plane of metals and established as binuclear complex $L_2Cu_2Cl_2$, bounded through two chlorine atoms. The ligands are practically coplanar and rotated 180 degrees to each other. The coordination geometry of the copper(II) atoms is distorted triangular bipyramid. The metal atom is surrounded by two chloride anions, aldimine nitrogen atom, sulfur atom of the thiolate group and keto-group of the pyrone ring. The corresponding donor atoms and copper atom form two practically coplanar 5-and 6-membered metallacycle. The arylamide fragment is slightly disordered. The plane formed by the atoms of chlorine and copper is a distorted square almost perpendicular to the plane of the ligands, with a deviation of 3.65 °

3.3. Electrochemistry

Some of the obtained ligands and complexes were studied by means of cyclic voltammetry (CV) using a glass carbon (GC) electrode in DMF, to determine the potential participation of compounds in oxidation-reduction processes. The potentials of electrochemical oxidation and reduction are given in Table 2.

All investigated ligands undergo three-step reduction on GC electrode at potentials in the range -0.93 - -2.04 V (the only exception is the compounds **6b**, which undergo two-step reduction, see Table). Most ligands are characterized by irreversibility of reduction steps, except the phenol- containing compounds **6d**, with a reversible reduction on the first step. Ligands oxidation proceeds in two irreversible steps at the potentials 0.94 - 1.68 B (Table2, Fig.2).

The performed semi-empirical PM3 calculation for the ligands showed that their HOMO are mainly localized on the arylamido-fragment. At the same time, the conjugated chromonohydrazone system makes a significant contribution to the LUMO (Table 3). Based on this results, we can assume that the oxidation potentials of the compounds **6a**, **b**, **d**, **g**, **l** will be

mainly influenced by the substituents in the benzene ring, and the reduction potentials – by the chromone fragment substituents.

The values of the measured oxidation and reduction potentials are confirmed by the calculated data: thus, the values of the first oxidation potentials of the compounds. **6a**, **d**, **g**, having various chromone substituents and the same benzamide moiety, are within the range 0.95-1.12 V, i.e. differ by no more than 0.17 V. At the same time, for the compounds **6a**, **1** and **6b** with the substituents of different nature (donor and acceptor) in the arylamide fragment, the first oxidation potentials differ considerably (in the range 0.92-1.17 V, the potential range is of 0.25 V). As expected, the donor substituents (OMe) of aromatic fragments facilitate oxidation, and acceptor (F) impede it (Table 2).

On the CVA curves of copper complexes two additional quazy-reversibly one-electronic peaks are observed in addition to the ligand peaks (Table and supplementary). These peaks are in the less negative potential region then the first peak of the free ligand, and presumably correspond to $Cu^{II}Cu^{II} \rightarrow Cu^{I}Cu^{II}$ and $Cu^{I}Cu^{II} \rightarrow Cu^{I}Cu^{I}$ transitions. The peaks of oxidative desorbtion of metal copper from the electrode surface was not observed on the CVA reverse scan after these peaks, this indicates the stability of the reduced forms of complexes (Fig.2, Table 2).

Oxidation of the copper-containing complexes proceeds irreversibly in two or three steps. Apparently, the oxidation of the coordinated ligand fragment takes place, as the shape of the CV curves and the potentials of the oxidation peaks slightly differ from the free ligands curves. The shift of oxidation potentials of the complexes to the lower potentials is presumably due to coordination with positively charged metal ion.

The cobalt-containing complexes 7e, 7b, and 7y (the first reduction peaks at $E_{red} = -0.69$; -0.69; -0.83 V; and the second reduction peaks at $E_{red} = -1.36$; -1.36; -1.37 V respectively) and nickel containing complex 7c are presumably reduced initially to the metal, then to the ligand in accordance with the scheme $L_2Cl_2Co^{II}Co^{II} \rightarrow L_2Cl_2Co^{IC}O^{II} \rightarrow L(L^-)Cl_2Co^{IC}O^{II}$.

Thus, in accordance with electrochemical behavior two types of cobalt and nickel complexes can be distinguished: cobalt complexes of phenolic ligands **6a**, reduced to the metal, and other complexes, which are reduced to the metal at the first step, and to the coordinated ligand fragment at the second .Oxidation of cobalt and nickel complexes, as well as oxidation of copper complexes, apparently proceeds to the ligand fragment.

The semi-empirical calculation of the frontier orbitals for complexes shows that the HOMO and the LUMO of the molecules, as well as ligand molecules, are mainly located on the C=S fragment. However, while for Cu and Ni complexes the HOMO is also localized on the metal atom, for Co complexes the contribution of metal atoms to the HOMO is much smaller (Table 3), which makes preferable the electron to the coordinated ligand fragment.

Table 2. Electrochemical reduction potentials (E_{Red}) and oxidation potentials (E_{Ox}) of the ligands 6a, b, d, g, l and their metal complexes measured relative to Ag|AgCl|KCl(sat.) by the CV methods at a glassy-carbon electrode (DMF, 0.05 M Bu4NClO4, 200 mV s⁻¹). The values after the slash marks represent the peak potentials for the reverse CV scans.

Compound	$E_p^{\rm red}, { m V}$	$E_p^{\text{ox}}, \mathbf{V}$
ба	-1.65	0.96
O NH-N NH	-1.80	1.68
	-1.97	
~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~	6	
$(6a - H)_2Cu_2Cl_2$ (complex7a)	-0.12/-0.08	0.78
	-0.68/-0.54	0.93
	-1.63	
$(6a - H)_2Co_2Cl_2$ (complex7b)	-0.69	1.10
	-1.36	1.28
	-1.92	1.64
	-0.81	0.69
$(6a - H)_2Ni_2Cl_2$ (complex7c)	-1.40	0.90
	- 1.94	1.60
6b	-1.78	1.17
O NH-N NH	-1.94	1.44
	-0.19/-0.08	0.82
	-0.75/-0.67	0.96 1.09
$(6b - H)_2Cu_2Cl_2$ (complex 7d)	-1.71	
	-1.87	
	-0.69;	1.09
$(0\mathbf{D} - \mathbf{H})_2 \mathbf{C}0_2 \mathbf{C}\mathbf{I}_2 \text{ (complex 7e)}$	-1.36;	
	-1.92	
$(6b - H)_2Ni_2Cl_2$ (complex 7f)	-0.76;	1.00;

	-1.11;	1.32;
	-1.40;	1.66
	-1.88	
6d	-1.17/-1.11	0.95
	-1.73/-1.57	1.45
	-2.04	
χ γ γ s ö		
HO		
(6d-H) ₂ Co ₂ Cl ₂ (complex 7h)	-1.26/-1.18	0.97
	-1.66	1.35
	-1.84	
6g	-1.47	1.12/-0.93
	-1.75	
	-1.97	
Y Y Y S O		
	0.31/0.39	0.85/0.74
$(6g - H)_2Cu_2Cl_2$ (complex 7i)	-1.35/-1.20	1.08
	-1.76	
	-2.14	
61	-1.66	0.92
	-1.81	1.36
O NH OMe	- 1.99	
()	0.04/0.55	1.04
(6) H) $Cu Cl (complex 7x)$	-0.52/-0.45	1.45
$(\mathbf{u} - \mathbf{n})_2 \subset \mathbf{u}_2 \subset \mathbf{u}_2 (\text{complex } / \mathbf{v})$	-1.52	
	-1.65	
	-1.90	
	-0.83	1.28
$(\mathbf{0I} - \mathbf{H})_2 \mathbf{C} 0_2 \mathbf{C} \mathbf{I}_2 \text{ (complex 7x)}$	-1.37	
	-1.76	
$(6l - H)_2Ni_2Cl_2$ (complex 7y)	-0.93	0.90



Table 3. HOMO and LUMO of ligand 6a and its copper complex 7a.



**Fig 2.** Cyclic voltammograms of ligand **6b** (a) and its copper complex **7d** (b), cobalt complex **7e** (c), nickel complex **7f** (d). DMF, 0.05 M Bu₄NClO₄,  $10^{-3}$  M.

#### 4. Conclusion

In the conclusion, a series of binuclear copper(II), cobalt(II) and nickel(II) complexes with novel organic ligands 2-oxo-2-(arylamino)-(2*E*)-2-[(4-hydroxy-2-oxo-2H-1-benzopyran-3-yl)-methyledene]ethanethioic acid hydrazides, forming as a result of 3-formylchromones and oxamic acid thiohydrazides interaction, have been prepared by the reactions of metal chloride with ligand in EtOH. The complexes have been characterized by IR, UV–vis spectroscopy and cyclic voltammetry. Unexpected cyclic forms of the ligands, namely 5-(4-oxo-4H-chromen-3-yl)-4,5-dihydro-1,3,4-thiadiazole-2-carboxamides, have been determined as preferable tautomers in the solution and solid. The X-ray analysis of di- $\mu$ -chloro-bis-(((Z)-2-oxo-1-((E)-((4-oxo-4H-chromen-3-yl))methyledene)hydrazono)-2-(phenylamino)ethyl)thio)dicopper(II)distorted triangular bipyramid geometry with an OSNCl₂ donor set.

#### Appendix A. Supplementary data

CCDC 1575758 contains the supplementary crystallographic data for 7a. These data can be obtained free of charge via http://www.ccdc.cam.ac.uk/conts/retrieving.html, or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: (+44) 1223-336-033; or e-mail: deposit@ccdc.cam.ac.uk.

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A series of 5-(4-oxo-4H-chromen-3-yl)-4,5-dihydro-1,3,4-thiadiazole-2-carboxamide and copper(II), cobalt(II) and nickel(II) complexes of their tautomers 2-oxo-2-(arylamino)-(2*E*)-2-[(4-hydroxy-2-oxo-2H-1-benzopyran-3-yl)methyledene]ethanethioic acid hydrazides have been synthesized.