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Synthesis, spectroscopy and magnetism of novel metal complexes of 3-aminoflavone (3-af). X-ray crystal structure of 3-af and $[Cu(3\text{-}af)_2(NO_3)_2]$

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ABSTRACT

The synthesis and characterization of four new complexes with the bioactive ligand 3-aminoflavone (3-af) are reported. The complexes of general formula $[M(3\text{-}af)_2(H_2O)_2](NO_3)_2 \cdot nH_2O]$, where M = Co(II), Ni(II), and Zn(II), and $n = 0, 2, 0$, respectively, and $[Cu(3\text{-}af)_2(NO_3)_2]$ compound were prepared and studied. In particular, to investigate the binding in detail, the crystal structures of the free ligand (3-af) and $[Cu(3\text{-}af)_2(NO_3)_2]$ (**1**) were determined. The new coordination compounds were identified and characterized by elemental analysis, magnetic measurements, and infrared and ligand-field spectra. The crystal structure of the Cu(II) complex reveals that the ligand acts as a *N*,*O*-bidentate chelate ligand forming a five-membered ring with the copper(II) ion. The copper(II) ion is octahedrally surrounded by the two amino nitrogens and two carbonyl oxygens from two chelating organic ligands in *trans* arrangement. Two molecules of coordinated nitrate anions occupy axial positions. The spectral and magnetic properties are in accordance with the structural data of the copper(II) compound. From X-ray powder-diffraction patterns and IR spectra, the complexes of nickel(II) (**2**) and cobalt(II) (**3**) were found to be mutually isomorphous. The results of the spectroscopic studies suggest a mononuclear structure of **2** and **3** complexes. The variable-temperature (1.8–300 K) magnetic susceptibility data of **2** indicate a weak ferromagnetic interaction. The magnetic behavior of complex **3** is characteristic of cobalt(II) systems with an important orbital contribution via spin–orbit-coupling and also suggests a weak ferromagnetic interaction.

1. Introduction

Flavonoids are a very important group of bioligands and their activity is well recognized, e.g. as antiviral, antibacterial, cytostatic and naturally occuring antioxidants. The flavonoid ligands themselves have anticancer activity as they are more toxic in cancer cells than in normal ones [1,2]. In the course of search for new antitumor agents the synthetic derivatives of flavone, the ring system which belongs to the flavonoids, were intensively examined. In a previous study, we have reported the results of the synthesis, spectroscopy and *in vitro* alkylating activity of the platinum(II) and palladium(II) complexes of oximes of flavanone and their *O*-methyl ethers [3]. *cis*-Pt(II) complex of 3-aminoflavone (3-af), *cis*-bis(3-aminoflavone)dichloridoplatinum(II) (*cis*-BAFDF) is structurally related to *cis*-DDP, containing a flavone molecule instead of the ammine with two *cis* bound labile chlorido ligands [4]. This compound exhibited significant antitumor activity against the development of leukemia L1210 cells in mice and cytotoxicity was tested by measuring the inhibitory effect on L1210 cell proliferation [5,6]. The new analogue induced apoptosis and necrosis and showed a weaker genotoxicity than cisplatin [7,8]. It has been proved that the new analogue induced a higher percentage of *P*53 and *BAX* expressions in A549 cells in comparison with *cis*-DDP [9]. Moreover, the *cis*-Pt(II) complex of 3-aminoflavone showed a weaker genotoxic effect in normal lymphocytes in comparison with *cis*-DDP, which was found to be a stronger inducer of apoptosis and necrosis [10].

Metal ions relevant in biology have been chosen for the present investigation of 3-af. Copper and zinc compounds are widely used in biochemistry (enzymes) and medicine; nickel is an essential trace element present in many hydrogenases and cobalt as constituent of vitamin B_{12} (which is necessary for the synthesis of nucleic acids) are essential in living systems. Besides, the copper ion as a component of novel organic complexes was found as a promising metal in relation to their antitumor activity [11,12]. Recently, copper complexes of 2-furaldehyde oxime have been found to exhibit higher cytotoxic activity against murin and inhibit L1210 lymphoid leukemia DNA in comparison to etoposide [13]. Other research has

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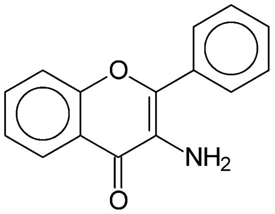

Fig. 1. Lewis formula of the ligand 3-aminoflavone.

shown that a copper complex with tetrabenzotetraazacyclohexadecine ligand is a promising compound against the melanoma B16 and leukemia P388 [14,15]. There are some copper compounds, that exhibit antiproliferative activity by themselves [16,17].

3-Aminoflavone (3-af) (Fig. 1) as a synthetic bioligand contains both O (carbonyl) and N (amine) sites to form chelate complexes as resulted from X-ray crystal structure of $[Cu(3\text{-af})_2(ClO_4)_2]$ as was presented by us earlier [18]. Here, we are interested in the synthesis of nitrate transition metal complexes (M = Cu(II), Ni(II), Co(II), Zn(II) ions) of 3-af. In this paper, we present the synthesis, spectroscopic and magnetic properties (for paramagnetic ions) of $[Cu(3\text{-af})_2(NO_3)_2]$ (**1**), $[Ni(3\text{-af})_2(H_2O)_2](NO_3)_2 \cdot 2H_2O$ (**2**), $[Co(3\text{-af})_2(H_2O)_2](NO_3)_2$ (**3**) and $[Zn(3\text{-af})_2(H_2O)_2](NO_3)_2$ (**4**) compounds. Additionally, the coordination compounds have been characterized by powder diffractometry. For $[Cu(3\text{-af})_2(NO_3)_2]$ (**1**) compound, the X-ray crystal structure has been determined.

2. Experimental

2.1. Reagents and physical measurements

Melting points were determined with a Beathius apparatus and have not been uncorrected. Elemental analyses were carried out using Perkin Elmer PE 2040. Infrared spectra were recorded on a Bruker IFS 113v spectrometer and Infinity MI 60 series FTIR using KBr pellets and solid-state electronic spectra (28000–4000 cm^{-1}) on a Cary 500 spectrophotometer. ^1H NMR spectra were recorded with Tesla BS-567A spectrometer (300 MHz), chemical shifts (δ) are reported in ppm in respect to TMS as an internal standard.

EPR spectra of the polycrystalline samples were recorded at X-band at room temperature and 77 K on an ESP 300E Bruker spectrometer with an ER 035M Bruker NMR Gaussmeter and a Hewlett Packard microwave frequency counter.

Magnetic susceptibility measurements were carried out on solid polycrystalline samples with a Quantum Design SQUID magnetometer (type MPMSXL-5). Measurements were recorded at a magnetic field of 0.5 T in the temperature range 1.8–300 K. Corrections were based on subtracting the sample holder signal and estimating the contribution χ_D from the Pascal constants [19]. The effective magnetic moments were calculated from $\mu_{eff} = 2.83(\chi_M T)^{1/2}$ using temperature-independent paramagnetism (TIP) of $60 \times 10^{-6}\ cm^3\ mol^{-1}$, $220 \times 10^{-6}\ cm^3\ mol^{-1}$ and $150 \times 10^{-6}\ cm^3\ mol^{-1}$ for Cu(II), Ni(II) and Co(II), respectively [20].

X-ray powder-diffraction patterns were collected at room temperature using PANalytical X'Pert Pro MPD diffractometer with the copper long line fine focus X-ray tube and the PANanalitical X'Celerator detector based on the real time multiple strip technology. The latter is capable of simultaneously measuring the intensities within the O range of 2.122°. Divergent optics in a Bragg–Brentano (flat-plate sample) geometry with fixed divergence and antiscatter slits was applied. Additionally incident and receiving 0.04 rad Soller slits were used to limit axial divergence and a nickel filter on the receiving side was applied to eliminate Cu Kβ radiation. Data were collected in the range $4° < O < 35°$ with the scan width 0.0167° and scan exposition 20 s.

2.2. Crystal structure determination of 3-af and $[Cu(3\text{-af})_2(NO_3)_2]$ (1)

Crystal data of 3-af and $[Cu(3\text{-af})_2(NO_3)_2]$ (**1**) were collected at room temperature on an Enraf-Nonius-KappaCCD diffractometer using graphite-monochromated Mo Kα radiation ($\lambda = 0.71069$ Å). For data reduction and cell refinement the programs DENZO and SCALEPACK were used [21]. The structure was solved by conventional Patterson methods for (**1**) or direct methods for (3-af) and subsequent Fourier syntheses and refined by full-matrix least squares on F^2 using the SHELXTL-PLUS and SHELXL-93 programs [22]. The scattering factors were those given in the SHELXTL-PLUS program. All non-hydrogen atoms were refined with anisotropic displacement parameters. Hydrogen atoms in **1** were located in the Fourier-difference map and refined isotropically. In the structure of free 3-af ligand hydrogen atoms were generated geometrically and given fixed isotropic thermal parameters in order to save parameters. Crystallographic data and details of refinement for 3-af and $Cu(3\text{-af})_2(NO_3)_2$ (**1**) are reported in Table 1.

2.3. Synthesis of 3-af and complexes 1, 2 and 3

The starting compound flavanone was purchased from Sigma–Aldrich CO (St. Louis, MO, USA). 3*Z*-Hydroxyiminoflavanone was prepared according to the procedure described elsewhere [23,24]. Infrared spectra of KBr pellets were measured with an ANTI MATTSOM IFS FT spectrometer.

2.3.1. 3-Aminoflavone (3-af)

To the solution of 3*Z*-hydroxyiminoflavanone (3.0 g, 1.2 mmol) in a glacial acetic acid (72 mL) with concentrated hydrochloric acid (12 mL), $SnCl_2$ (6.0 g, 3.2 mmol) was added. The mixture was vigorously stirred at room temperature for 6 h. After this time the precipitate was filtered off, washed with water to pH about 7 and recrystallized from methanol to give 3-aminoflavone (3-af) as yellow needles (2.3 g, yield 78% m.p. 138–139 °C) [24]. Calc. for $C_{15}H_{11}NO_2$ (m.mol. 237.25): C, 75.94; H, 4.67; N, 5.90. Found: C, 75.78; H, 4.51; N, 5.85%.

Table 1
Crystal data and structure refinement for 3-af and $Cu(3\text{-af})_2(NO_3)_2$ (**1**)

	3-af	**1**
Formula	$C_{15}H_{11}NO_2$	$C_{30}H_{22}CuN_4O_{10}$
Fw	237.25	662.06
Crystal habit	colorless needle	green block
Crystal dimensions (mm)	0.10 × 0.10 × 0.3	0.12 × 0.15 × 0.21
Crystal system	monoclinic	triclinic
Space group	$P2_1/n$	$P\bar{1}$
a (Å)	3.887(1)	5.450(1)
b (Å)	22.007(1)	11.125(1)
c (Å)	13.199(1)	12.092(1)
α (°)		102.43(1)
β (°)	97.32(1)	100.35(1)
γ (°)		98.64(1)
V (Å^3)	1119.9(3)	690.6(2)
Z	4	1
$F(000)$	496	339
λ (Å)	0.71069	0.71069
$\rho_{calc.}$ ($g\ cm^{-3}$)	1.407	1.592
μ(Mo Kα) (mm^{-1})	0.094	0.86
Reflections collected/unique (R_{int})	6492/2204 (0.066)	6340/1646 (0.045)
Observed reflections[a]	980	1445
Parameters	163	249
R_1[a,b]	0.042	0.037
wR_2[a,c]	0.087	0.099
(Δ/ρ) maximum/minimum (e Å^{-3})	0.240/−0.173	0.280/−0.431

[a] Observation criterion: $I > 2\sigma(I)$.

[b] $R_1 = \sum||F_o| - |F_c||/\sum|F_o|$.

[c] $wR_2 = \left[\sum w(F_o^2 - F_c^2)^2 \big/ \sum w(F_o^2)^2\right]^{1/2}$.

2.3.2. *[Cu(3-af)$_2$(NO$_3$)$_2$] (**1**)*

To the solution of 3-af (237 mg, 1 mmol) in methanol (20 mL), copper nitrate (148 mg, 0.5 mmol) was added. The mixture was vigorously stirred at room temperature for 4 h. The microcrystalline powder of complex was filtered off and recrystallized from methanol giving a dark-green complex (m.p. 179–181 °C prisms). Yield: 280 mg (85%). Selected IR data (KBr, cm^{-1}) ν: 3424 (H_2O); 3062, 3024 (NH_2); 1621 (CO); 1408, 1298 (NO_3). Calc. for $C_{30}H_{22}CuN_4O_{10}$ (m.mol. 661.8): C, 54.44; H, 3.32; N, 8.46. Found: C, 54.18; H, 3.41; N, 8.40%.

2.3.3. *[Ni(3-af)$_2$(H$_2$O)$_2$](NO$_3$)$_2$ · 2H$_2$O (**2**)*

To the solution of 3-af (237 mg, 1 mmol) in dry ethyl acetate (50 mL), nickel nitrate (146 mg, 0.5 mmol) was added. The reaction mixture was stirred under reflux for 6 h. The microcrystalline powder of complex was filtered off and washed with dry diethyl ether (m.p. 273–276 °C). Yield: 260 mg (71%). Selected IR data (KBr, cm^{-1}) ν: 3424 (H_2O); 3295, 3233 (NH_2); 1621 (CO); 1408, 1384, 1317 (NO_3). Calc. for $C_{30}H_{30}NiN_4O_{14}$ (m.mol. 729.0): C, 49.42; H, 4.11; N, 7.68. Found: C, 49.06; H, 3.88; N, 7.91%.

2.3.4. *[Co(3-af)$_2$(H$_2$O)$_2$](NO$_3$)$_2$ (**3**)*

To the solution of 3-af (237 mg, 1 mmol) in dry ethyl acetate (50 mL), cobalt nitrate (146 mg, 0.5 mmol) was added. The reaction mixture was stirred under reflux for 6 h. The microcrystalline powder of complex was filtered off and washed with dry diethyl ether (m.p. 222–226 °C). Yield: 270 mg (78 %). Selected IR data (KBr, cm^{-1}) ν: 3424 (H_2O); 3306, 3236 (NH_2); 1621 (CO); 1408, 1384, 1317 (NO_3). Calc. for $C_{30}H_{26}CoN_4O_{12}$ (m.mol. 693.3): C, 51.97; H, 3.75; N, 8.08. Found: C, 51.77; H, 3.49; N, 8.19%.

2.3.5. *Zn[(3-af)$_2$(H$_2$O)$_2$](NO$_3$)$_2$ (**4**)*

To the solution of 3-af (237 mg, 1 mmol) in dry ethyl acetate (50 mL), zinc nitrate (149 mg, 0.5 mmol) was added. The reaction mixture was stirred under reflux for 6 h. The microcrystalline powder of complex was filtered off and washed with dry diethyl ether (m.p. 225–229°C). Yield: 230 mg (67%). Selected IR data (KBr, cm^{-1}) ν: 3433 (H_2O); 3206, 3059 (NH_2); 1621 (CO); 1406, 1384, 1293 (NO_3). Calc. for $C_{30}H_{26}ZnN_4O_{12}$ (FW 699.9): C, 51.48; H, 3.74; N, 8.12. Found: C, 51.39; H, 3.66; N, 8.16%. ^1H NMR (DMSO-d_6) δ: 4.73 (s, 4H, NH_2, disappear in D_2O), 7.41–7.79 (m, 12H, arom.), 7.97 (d, 4H, arom.), 8.10 (dd, 2H–C_5).

The attempts of the preparation of Co(II), Ni(II) and Zn(II) compounds were unsuccessful so far.

3. Results and discussion

We have synthesized a series of M(II) nitrate complexes with 3-aminoflavone (3-af) ligand. The stoichiometry of the investigated complexes was established from the elemental analysis. The analytical results demonstrated that the 3-af ligand forms coordination compounds of formula [Cu(3-af)$_2$(NO$_3$)$_2$] (**1**), [Ni(3-af)$_2$(H$_2$O)$_2$](NO$_3$)$_2$ · 2H$_2$O (**2**), [Co(3-af)$_2$(H$_2$O)$_2$](NO$_3$)$_2$ (**3**) and Zn[(3-af)$_2$(H$_2$O)$_2$](NO$_3$)$_2$ (**4**). Single X-ray crystal studies of [Cu(3-af)$_2$(NO$_3$)$_2$] (**1**) compound were undertaken to elucidate the coordination sphere of copper(II). The nickel, cobalt and zinc compounds were found as structurally almost isomorphous, because their X-ray powder patterns are identical (Fig. 2).

3.1. *Description of the structure of AF and [Cu(3-af)$_2$(NO$_3$)$_2$] (**1**)*

Crystal data of 3-af and copper(II) compound (**1**) are summarized in Table 2, relevant bond lengths and angles for **1** are listed in Table 1. The molecular structures of the free 3-af ligand and of [Cu(3-af)$_2$(NO$_3$)$_2$] are depicted in Figs. 3 and 4.

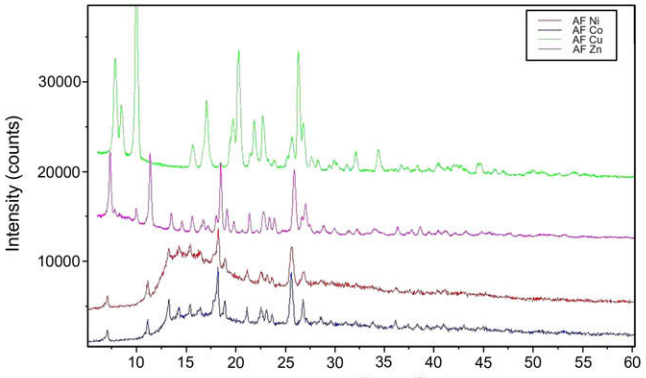

Fig. 2. X-ray powder diffractograms of 3-af complexes.

The crystal packing of the free ligand is stabilized by one weak intermolecular hydrogen bond C(4)–H(4)···O(2) ($-1/2 + x$, $1/2 - y$, $1/2 + 2$) [C(4)···O(2) 3.229(3) Å]. Additionally, aromatic π–π stacking interactions between molecules along x-axis are observed. The distance between respective ring centroids is 3.586(2) Å (Fig. 5).

In **1** the 3-aminoflavone (3-af) ligand chelates the copper atom, forming a five-membered ring. The intraligand geometry is normal in this structure and compares well with that of the free ligand. The copper atom is surrounded by six symmetrically related atoms, namely two carbonyl oxygens and two amino nitrogens from two 3-af ligands in the basal plane in *trans* conformation, and, at longer distances, two oxygen atoms from two nitrate anions in axial positions. The length of the Cu–O (from nitrate anions) bond, being 2.427(3) Å is significantly longer compared with those between Cu and the ligand donor atoms, which are 1.973(2) (Cu–O) and 1.986(3) Å (Cu–N), respectively, which causes a significant distortion of the coordination polyhedron around the Cu(II) ion. Therefore, the polyhedron can be described as a tetragonally distorted octahedron symmetrically elongated along Cu–O (from coordinated nitrate groups) direction. The values observed for the Cu–N and Cu–O distances are within reasonable bonding distances and comparable with similar CuN_2O_4 chromophores [25–28]. The C=O bond lengths in **1** and in the free ligand are equal within the experimental error (1.254(4) Å in **1**, 1.244(2) Å in AF) and consistent with a C=O double bond. However, Cu coordination moves the exocyclic oxygen slightly out of the ring plane (distance to the best-weighted plane 0.224(4) Å in **1** versus 0.004(2) Å in 3-af). The exocyclic nitrogen is coplanar with the ring plane (distance to the best-weighted plane 0.022(5) Å for **1**, 0.034(2) Å for AF). Binding of Cu leads to an increase in the C–N bond length of about 0.04 Å 1.437(4) Å in **1**, 1.396(2) in free 3-af. In **1**, a twist angle of 39.2(1)° is observed between the phenyl ring and the heterocyclic ring which compares well with that found in the free ligand (40.66(4)°). The nitrate anion has its expected planar trigonal geometry. The nitrogen–oxygen bond lengths and intraanion bond angles are average (1.220–1.268 Å) and (119.1–121.1°). The amino group of 3-af forms an intramolecular hydrogen bond with nitrate oxygen (N(1)···O(5a) 2.875(4), N(1)···H···O(5a), 167(4)°, $-x$, $-y$, $-z$). In the crystal packing, molecules stack along the x-axis with stacking distances between 3-aminoflavone moieties being 3.8 Å

Table 2
Selected bond lengths (Å) and angles (°) in [Cu(3-af)$_2$(NO$_3$)$_2$] (**1**)

Cu(1)–N(1)	1.986(3)
Cu(1)–O(2)	1.973(2)
Cu(1)–O(3)	2.427(3)
N(1)–Cu(1)–O(2)	85.0(1)
O(2)–Cu(1)–O(3)	95.3(1)
N(1)–Cu(1)–O(2)[a]	95.0(1)

[a] Symmetry operation: $-x$, $-y$, $-z$.

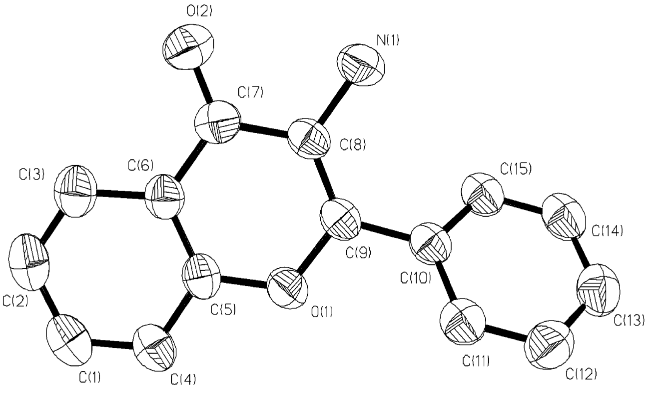

Fig. 3. Molecular structure and labeling scheme of 3-af.

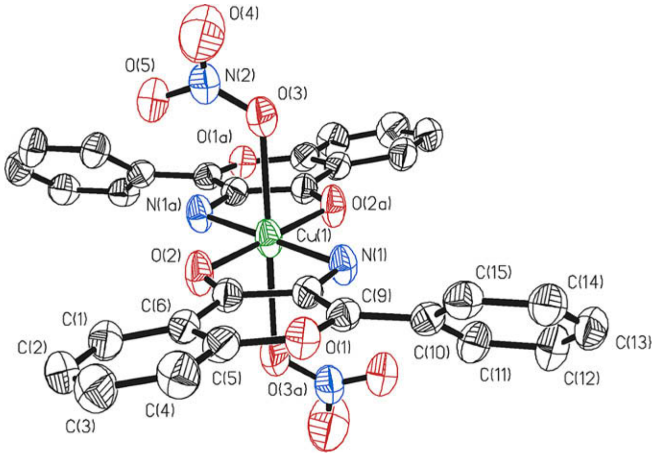

Fig. 4. The molecular structure and labeling scheme of $[Cu(3\text{-af})_2(NO_3)_2]$ (**1**). Hydrogen atoms are omitted for clarity.

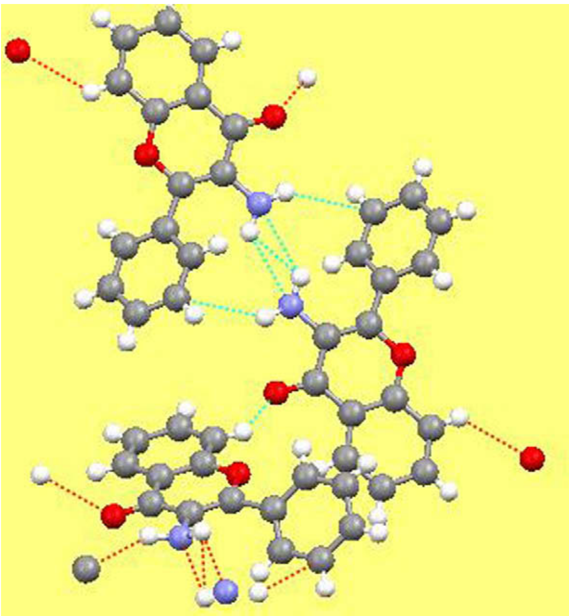

Fig. 5. Crystal packing of 3-aminoflavone. Hydrogen bonds are shown with dashed line.

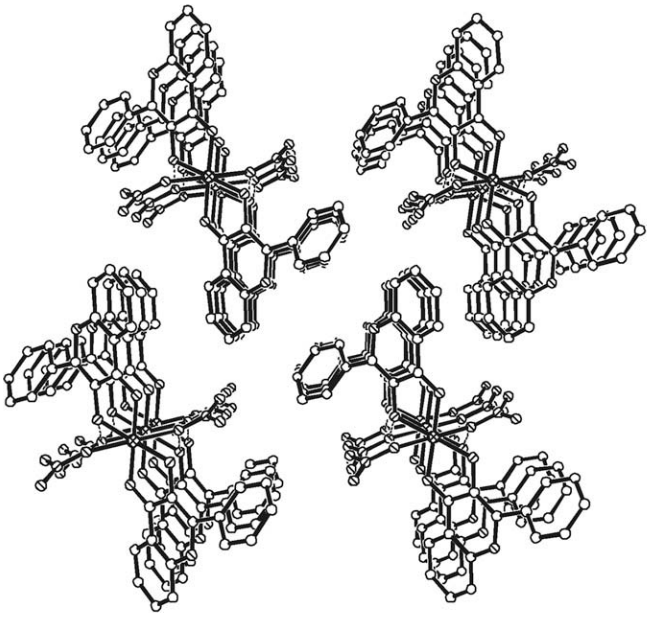

Fig. 6. Crystal packing of $[Cu(3\text{-af})_2(NO_3)_2]$ (**1**) viewed along the x-axis.

(Fig. 6). Intermolecular hydrogen bonds are formed between the amino group of 3-af and nitrate oxygen (N(1)···O(3), 2.865(5) Å, $1 - x, -y, -z$). Quite similar arrangement has been found in already reported isostructural *trans*-$Cu(3\text{-af})_2(ClO_4)_2$ complex [18] in which central copper atom is significantly deformated towards a tetragonal bipyramid in which perchlorate oxygen atoms occupy apical positions.

3.2. Spectroscopic properties

The infrared spectrum of **1** shows NO_3 bands at 1299 and 1408 cm^{-1} typical for unidentate coordination of the nitrate ion, which is confirmed by the structure determination [29]. The infrared spectra of **2**, **3** and **4** show a very strong band at about 1384 cm^{-1}, characteristic of an ionic nitrate [29]. Compounds **2**, **3** and **4** exhibit in the O–H stretching region, a strong and sharp absorption at about 3430 cm^{-1} due to coordinated water molecule involved in the O···H hydrogen bond, while the IR spectrum of **1** shows the absence of all vibrations that might be attributed to the presence water. Compounds **2**, **3** and **4** exhibit two sharp absorptions, respectively, associated [30] with the NH_2 groups (**2**: 3295, 3233 cm^{-1}, **3**: 3306, 3236 cm^{-1}, **4**: 3206, 3059 cm^{-1}). For **1** ν_{NH} is at 3020sh, 3063 cm^{-1}. The ligand exhibits two ν_{NH} stretching frequencies (3314, 3404 cm^{-1}) associated with NH_2 groups in 3-af. The absorption band at 1621 cm^{-1}, which corresponds to C═O stretching and these associated with NH_2 group of the free ligand are shifted towards lower frequencies, suggesting their participation in coordination of the metal ions.

The ligand-field spectrum of **1** shows a broad asymmetric band with maximum centered at 15 720 cm^{-1} indicating an elongated octahedral geometry for the copper ion which is confirmed by the structure determination. The ligand-field spectra of **2** (16 610, 10 470 cm^{-1}) and **3** (20 570, 9470 cm^{-1}) are typical for octahedral high-spin complexes of these divalent metal ions [31]. The spectrochemical parameters calculated are $10Dq = 10\,470\ cm^{-1}$ for **2** and $10Dq = 10\,350\ cm^{-1}$, $B = 820\ cm^{-1}$ for **3** [32,33]. The values of Dq determined for Ni(II) and Co(II) complexes are in good agreement with those expected for isomorphous nickel and cobalt compounds and with MN_2O_4 chromophore [32,33]. The rather high value of B for **3** may suggest a distorted octahedral geometry [31]. For **2** the B value cannot be calculated because the highest energy triplet–triplet transition is not observed, masked by strong UV absorption. The $10Dq$ values for both complexes show that the nearest coordination sphere produces a strong ligand field. Asymmetric bands in the near-IR region of **2** and **3** show that the nickel(II) and cobalt(II) ions are in a tetragonally distorted N_2O_4 environment.

The X-band EPR spectrum of the polycrystalline sample of $[Cu(3\text{-af})_2(NO_3)_2]$ (**1**) is an axial type showing $g_{\parallel} = 2.37_5$ and $g_{\perp} = 2.04_0$ at r.t., and $g_{\parallel} = 2.37_9$ and $g_{\perp} = 2.04_6$ at 77 K. The hyperfine splittings are observed in room temperature and 77 K. The hyperfine splitting of the parallel component is well resolved with $A_{\parallel} = 160$ G. The observed $g_{\parallel}$ is a high for 3-af chelating ligand. This fact seems to indicate that the powder spectrum does not reflect molecular g value. There are no substantial differences between the spectra at the two temperatures. $[Ni(3\text{-af})_2(H_2O)_2](NO_3)_2 \cdot 2H_2O$ (**2**) compound does not exhibit any signal and $[Co(3\text{-af})_2(H_2O)_2](NO_3)_2$ (**3**) shows no lines at room temperature and only broad single line at 77 K at $g = 4.57$.

3.3. Magnetic properties

Variable-temperature (1.8–300 K) magnetic susceptibility data were collected for **1**, **2** and **3**. The magnetic behavior of complexes **1**, **2** and **3** is depicted in Fig. 7 in the form of $\chi_M T$ versus T, *respectively.*

The effective magnetic moment ($\mu_{eff} = 1.84\ \mu_B$) at room temperature for Cu(II) complex (**1**) is within usually observed range of experimental values for the copper(II) complexes in octahedral configuration [34]. The values of $\chi_M T$ are slightly dependent on the temperature and decreases only at the lowest temperature region (Fig. 7). The negative Weiss constant θ values of -0.62 K, obtained from the Curie–Weiss law [35] within the measured temperature region, suggest the possibility of a very weak antiferromagnetic interaction between magnetic centers inside crystal lattice in lower temperatures (see Section 3.1).

The value of $\chi_M T$ of **2** at room temperature is $1.56\ cm^3\ K\ mol^{-1}$ ($\mu_{eff} = 3.53\ \mu_B$), as compared to the expected spin-only value of $1.21\ cm^3\ K\ mol^{-1}$ for $S = 1$ with $g = 2.20$. The $\chi_M T$ value follows the quasi-Curie law from room temperature to 100 K: $\Theta = 8.3$ K and $C = 1.51\ cm^3\ K\ mol^{-1}$. At lower temperature it increases sharply to reach a maximum of $2.21\ cm^3\ K\ mol^{-1}$ at 12 K ($\mu_{eff} = 4.21\ \mu_B$) indicating weak ferromagnetic interaction. After the maximum, the $\chi_M T$ value decreases to $0.92\ cm^3\ K\ mol^{-1}$ at 1.8 K ($\mu_{eff} = 2.73\ \mu_B$) due to zero field splitting and/or weak antiferromagnetic coupling (Fig. 7).

Compound **3** exhibits the $\chi_M T$ value of $2.85\ cm^3\ K\ mol^{-1}$ ($\mu_{eff} = 4.77\ \mu_B$) at room temperature which is larger than that calculated for a spin quartet ($\chi_M T = 1.87\ cm^3\ mol^{-1}$ K, $3.87\mu_B$, for $S = 3/2$ with $g = 2.0$), but it agrees with the values observed for octahedral cobalt(II) complexes with a significant first-order orbital contribution to the magnetic moment typical for the $^4T_{1g}$ ground state [33,19]. The $\chi_M T$ plot (Fig. 7) gradually decreases with temperature and reaches the minimum value of $1.63\ cm^3\ K\ mol^{-1}$ ($\mu_{eff} = 3.61\ \mu_B$) at 1.8 K; therefore Co(II) ion remains totally high-spin down to 1.8 K. The $\chi_M T$ values follow the Curie–Weiss law from room temperature to 150 K with $C = 2.99\ cm^3\ K\ mol^{-1}$ and $\Theta = -1.7$ K. The value of -20 K is lower that expected for an isolated Co(II) with a spin–orbit constant of $-170\ cm^{-1}$ [19].

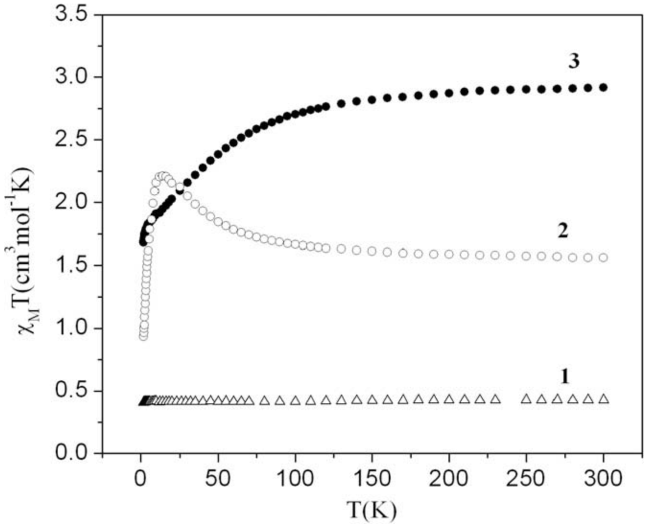

Fig. 7. Plot of $\chi_M T$ vs. T for (△) $Cu(3\text{-af})_2(NO_3)_2$ (**1**), (○) $[Ni(3\text{-af})_2(H_2O)_2](NO_3)_2 \cdot 2H_2O$ (**2**) and (•) $[Co(3\text{-af})_2(H_2O)_2](NO_3)_2$ (**3**).

Generally, the negative value of Θ for an isolated cobalt(II) ion is due to the overall effect of low-symmetry crystal-field components and spin–orbit coupling, resulting in a gradual transformation of an isotropic $S = 3/2$ at high temperature to an anisotropic effective $S = 1/2$ at low temperature. The calculated very small negative value of Θ (-1.7 K), which is lower than the expected value for an isolated Co(II), suggests an overall effect of the weak ferromagnetic interaction producing an increase of $\chi_M T$ values and of small antiferromagnetic exchange in the lowest temperature range, producing a decrease of $\chi_M T$ values. Because both **2** and **3** complexes have been found to be mutually isomorphous by X-ray powder determination, a ferromagnetic exchange interaction observed for **2** cannot be excluded between Co(II) centers in **2**.

Finally, on the basis of the spectroscopic properties of **2** and **3** compounds mononuclear structure is proposed. Unusual magnetic properties observed for these compounds clearly indicate magnetic exchange between metal centers. Probably these interactions occur within crystal lattice through H-bonds.

4. Conclusions

The bidentate 3-aminoflavone (3-af) ligand has been synthesized and its crystal structure has been determined. Attempts to prepare divalent copper, nickel, cobalt and zinc complexes were successful. In the mononuclear copper(II) complex the ligand forms a five-membered chelate ring with Cu, as inferred from the crystal structure of $[Cu(3\text{-af})_2(NO_3)_2]$ (**1**). The Cu(II) ion has a tetragonally distorted coordination sphere formed by two *N*,*O*-chelate ligands in *trans* arrangement and two nitrate ions.

So far it has not been possible to obtain single crystals suitable for X-ray measurement of **2**, **3** and **4** compounds, but the spectroscopic data indicate mutually similar distorted octahedral surroundings for the metal ions and monomeric structure. The unusual magnetic properties observed for **2** and **3** will deal with subsequent studies.

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Appendix A. Supplementary material

CCDC 637639 and 637638 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif. Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.ica.2008.04.014.

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