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Cobalt(III) Complexes with Biguanide Derivatives: Synthesis, Structures, and Antiviral Activity

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Abstract—Three Co(III) complexes with biguanide derivatives $[Co(NH_2C(=NH)NHC(=NH)NR^1R^2)_3]Cl_3$ ($R^1R^2 = Me_2$ (**I**), Et_2 (**II**), and H^sBu (**III**)) were obtained and characterized by elemental analysis, IR spectroscopy, and electronic absorption spectroscopy. Structure **III** was confirmed by X-ray diffraction (CIF file CCDC no. 1401783). Complexes **I**–**III** and $[M(SC(NH_2)_2)_4]Cl_2$ (M = Pd, Pt, and $[Co(En)_3]Cl_3$) were tested for in vitro antiviral activity against the A/California/07/09 (H1N1pdm09) influenza virus. The best results were achieved with complex **III** and both thiourea complexes.

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INTRODUCTION

The participation of many metal ions in the regulation of physiological processes motivated researchers to study metal complexes as therapeutic agents [1]. The biochemical effect of metal complexes is due to the preferred binding of positively charged metal centers to negatively charged biomolecules such as amino acid residues of proteins, ATP, and nucleic acids. In addition, the ligands coordinated to metal centers can also interact with biomolecules by forming hydrogen bonds as well as through dipolar interactions. The use of metal complexes as therapeutic agents has become increasingly important in the last few years; many promising drugs have been developed and are used against cancer, arthritis, ulcer, diabetes, anemia, and cardiovascular diseases [2].

It has been demonstrated that metal complexes can exhibit considerable biological activity if a metal cation (as an aqua complex) and a free ligand are both active [3]. Some other factors can also correlate with good antimicrobial and antiviral activity. These include (1) the presence in the ligand of uncoordinated (free) functional groups involved in the processes of recognition by a living organism and making the complexes more soluble; (2) the size and nature of substituents in the ligand that affect the lipophilicity of the complex, thereby controlling the penetration into a cell; (3) the presence of free coordination sites or labile ligands easy to be replaced in interactions with biomolecules; (4) stereochemistry, which can be favorable for interactions with the 3D structure of a biomolecule; (5) high kinetic and thermodynamic stability, which can prevent the ligand dissociation in the acidic environment of the stomach and the ligand metabolization in the blood as well as to ensure a low rate of ligand replacement by biomolecules present in the living cell.

Taking the aforementioned statements into account, we paid attention to cobalt complexes with substituted biguanides as potential antiviral drugs. Dimethylbiguanide itself is biologically active (an analgesic, an antimalarial and antimicrobial drug, a hypoglycemic agent in the treatment of diabetes, etc. [4–6]); in addition, its transition metal complexes also exhibit antimicrobial activity [7]. Another reason for our attention to transition metal complexes with biguanides is that cell infection with the influenza A virus is known to be triggered by acidification of the inner region of virus through proton transfer across the channel formed by protein M2 [8]. Anti-influenza agents such as amantadine and rimantadine act by blocking this channel via hydrogen bonging between the protonated imino group of the drug and a cluster consisting of structured water molecules and the histidine residues of the "histidine gate" in the channel of protein M2. The high efficacy of amantadine and rimantadine is also contributed by their adamantyl moiety that is complementary in size and shape to the M2 channel cavity immediately in front of the histidine gate. However, several recent influenza virus strains are nearly insensitive to rimantadine and amantadine since two amino acid residues in protein M2 of the mutated virus have been replaced to change the cavity shape of the channel. We expect that metal complexes with biguanide ligands will also be capable

Table 1. Crystallographic parameters and the data collection and refinement statistics for structure **III**

Parameter	Value
Molecular formula	$C_{18}H_{49}N_{15}O_2Cl_3Co$
M	673.00
Crystal system	Monoclinic
Space group	$P2_1$
a, Å	8.3057(4)
b, Å	21.7412(10)
c, Å	9.9072(4)
β, deg	113.306(1)
V, Å^3	1643.03(13)
Z	2
ρ_{calcd}, g/cm^3	1.360
$\mu_{MoK\alpha}$, mm^{-1}	0.808
Crystal dimensions, mm	0.30 × 0.14 × 0.10
F(000)	712
θ Scan range, deg	1.87–26.37
Ranges of h, k, l indices	$-10 \leqslant h \leqslant 10$, $-27 \leqslant k \leqslant 27$, $-12 \leqslant l \leqslant 12$
Number of measured reflections	19107
Number of unique reflections (R_{int})	6734 (0.0381)
Number of reflections with $I > 2\sigma(I)$	6285
Number of parameters refined	335
GOOF	1.048
R ($F^2 > 2\sigma(F^2)$)	$R_1 = 0.0608$; $wR_2 = 0.1652$
R (for all reflections)	$R_1 = 0.0638$; $wR_2 = 0.1679$
$\Delta\rho_{max}/\Delta\rho_{min}$, e Å^{-3}	0.967/0.797

of blocking the M2 channel but will be less sensitive to channel shape changes because of their many free amino groups.

The goal of this study was to obtain Co(III) complexes with substituted biguanides $[Co(NH_2C(=NH)NHC(=NH)NR^1R^2)_3]Cl_3$ (R^1R^2 = Me_2 (**I**), Et_2 (**II**), and H^{s}Bu (**III**)) and test them for antiviral activity against the A/California/07/09 (H1N1pdm09) influenza virus.

EXPERIMENTAL

IR spectra were recorded on a Scimitar FTS 2000 spectrometer. Electronic absorption spectra were recorded on a Shimadzu UV-3101PC spectrometer. Hydrochlorides of the biguanides $NH_2C(NH)NHC(NH)NR^1R^2$ (R^1R^2 = Me_2, Et_2, and H^{s}Bu) were prepared analogously to [9].

Synthesis of $[Co(NH_2C(NH)NHC(NH)NH^sBu)_3]Cl_3 \cdot 1.5H_2O$ (III). A solution of $Co(NO_3)_2 \cdot 6H_2O$ (291 mg, 1 mmol) in water (3 mL) was slowly added dropwise to a solution of $NH_2C(NH)NHC(NH)NH^sBu$ (650 mg, 3.65 mmol) and NaOH (336 mg, 8.4 mmol) in water (10 mL). The reaction mixture was stirred on a magnetic stirrer at room temperature for 30 min; the resulting light orange precipitate was decanted and washed with distilled water to a constant pH value. The product was suspended in water (10 mL); 30% H_2O_2 (2 mL) was added in small portions (1–3 drops) while vigorously stirring the suspension. The reaction mixture was stirred at room temperature for 20 min and then heated at 40°C for 30 min. After cooling to room temperature, the resulting dark brown solution was filtered through a paper filter. The filtrate was carefully acidified with dilute HCl to a neutral reaction, slowly concentrated with gentle heating (40–50°C) until crystallization began, cooled to room temperature, and kept at 5–8°C for 8 h. The dark red crystals that formed were collected on a Büchner funnel, washed with cold water and twice with cold ethanol, and dried on the filter in air. The yield of complex **III** was 358 mg (58%). Complexes **I** (47%) and **II** (53%) were obtained in a similar way.

X-ray diffraction study. The structure of complex **III** · $1.5H_2O$ was determined by X-ray diffraction on a Bruker-Nonius X8 Apex automated four-circle diffractometer equipped with a CCD area detector at 150(2) K according to a standard procedure (MoK_α radiation, λ = 0.71073 Å, graphite monochromator). An absorption correction was applied empirically from the intensities of equivalent reflections with the SADABS program [10]. The crystal structure of the complex was solved by a direct method. The H atoms of the ^{s}Bu-biguanide ligands were located geometrically and refined under rigid body constraints. The H atoms of water molecules were located in a difference electron-density map and refined using a riding model with $U_{iso} = 1.5U_{equiv}(O)$. Final refinement was carried out by the full-matrix least-squares method in the anisotropic approximation for all non-hydrogen atoms. All calculations were performed with the SHELXTL program package [10]. The structures were visualized with the DIAMOND program [11].

The crystallographic parameters and the data collection and refinement statistics for structure **III** are summarized in Table 1. Selected bond lengths and bond angles are listed in Table 2; the hydrogen bond parameters are given in Table 3. Atomic coordinates and thermal parameters have been deposited with the Cambridge Structural Database (CCDC no. 1401783; deposit@ccdc.cam.ac.uk or www.ccdc.cam.ac.uk/data_request/cif).

Table 2. Selected bond lengths (Å) and bond angles (deg) in structure **III**

Bond	*d*, Å	Angle	ω, deg
Co(1)–N(11)	1.914(4)	N(11)Co(1)N(12)	88.81(16)
Co(1)–N(12)	1.915(4)	N(21)Co(1)N(22)	88.64(17)
Co(1)–N(21)	1.914(4)	N(31)Co(1)N(32)	89.06(16)
Co(1)–N(22)	1.911(4)	N(11)Co(1)N(21)	90.11(17)
Co(1)–N(31)	1.918(4)	N(11)Co(1)N(22)	91.75(18)
Co(1)–N(32)	1.921(4)	N(11)Co(1)N(31)	177.4(2)
C(11)–N(11)	1.283(6)	N(11)Co(1)N(32)	88.80(18)
C(11)–N(13)	1.354(6)	N(12)Co(1)N(21)	177.9(2)
C(11)–N(14)	1.378(6)	N(12)Co(1)N(22)	89.64(17)
C(13)–N(12)	1.284(7)	N(12)Co(1)N(31)	89.85(17)
C(13)–N(14)	1.390(6)	N(12)Co(1)N(32)	91.75(18)
C(13)–N(15)	1.318(7)	N(21)Co(1)N(31)	91.29(17)
C(21)–N(21)	1.279(6)	N(21)Co(1)N(32)	89.98(18)
C(21)–N(23)	1.347(6)	N(22)Co(1)N(31)	90.42(17)
C(21)–N(24)	1.394(6)	N(22)Co(1)N(32)	178.5(2)
C(23)–N(22)	1.276(7)	N(11)C(11)N(14)	121.2(4)
C(23)–N(24)	1.386(6)	N(12)C(13)N(14)	121.4(5)
C(23)–N(25)	1.351(7)	N(21)C(21)N(24)	120.4(4)
C(31)–N(31)	1.288(6)	N(22)C(23)N(24)	121.7(4)
C(31)–N(33)	1.337(6)	N(31)C(31)N(34)	120.5(4)
C(31)–N(34)	1.383(6)	N(32)C(33)N(34)	121.6(4)
C(33)–N(32)	1.278(6)	C(11)N(14)C(13)	126.1(4)
C(33)–N(34)	1.381(7)	C(21)N(24)C(23)	124.6(4)
C(33)–N(35)	1.345(6)	C(31)N(34)C(33)	125.3(4)

Antiviral activity evaluation. Two techniques were used: (a) inhibition of the virus-induced cytopathic effect (CPE) [12] detected visually under a microscope and (b) neutral red uptake assay [13].

For this purpose, the MDCK cell culture was seeded in a 96-well plate (2×10^4 cells per well). The culture was incubated in an atmosphere of 5% CO_2 at 37°C for 20 h until 90% confluency was reached. Then the A/California/07/09 (H1N1pdm09) influenza virus was added in a dose of 100 $TCID_{50}$ per well. This dose is equivalent to the multiplicity of infection of 0.001 virus particles per cell. Thirty minutes after the infection, a test chemical sample was added to wells (C = 15–1000 μg/mL), and the wells were incubated under 5% CO_2 at 37°C for 72 h. Then the neutral red dye (the final concentration 0.34%) as an indicator was added to each well. After 1.5 h, a solution for dye extraction (0.1 M $NH_4H_2PO_4$ and 96% EtOH in equal volumes) was added to washed cells, and the optical density of the released dye at λ = 490 nm was measured. The antiviral activity of the complex was calculated as a dose (concentration) of the test sample that inhibits the viral replication by 50% (IC_{50}). Although we employed both the methods to calculate IC_{50} (CPE evaluation and neutral red uptake assay), only the dye uptake data are presented here because these are more objective.

In toxicity tests of the complexes, the MDCK cell culture was seeded in a 96-well plate (2×10^4 cells per well). The culture was incubated in an atmosphere of 5% CO_2 at 37°C for 20 h. Then the test complexes dissolved in MEM (Gibco) containing 5% FBS were added. After 72-h incubation, the percentage of cell proliferation inhibition was determined using neutral red as described above. Toxicity was calculated as a dose (concentration) of the test complex that causes the death of 50% cells (CD_{50}).

Complexes **I**–**III** and $[M(SC(NH_2)_2)_4]Cl_2$ (M = Pd (**IV**), Pt (**V**), and $[Co(En)_3]Cl_3$ (**VI**)) were tested for in vitro antiviral activity against the A/California/07/09 (H1N1pdm09) influenza virus. The data obtained are summarized in Table 4 (IS is the therapeutic index (selectivity index) defined as a ratio of the toxic dose to the inhibitory one: CD_{50}/ID_{50}).

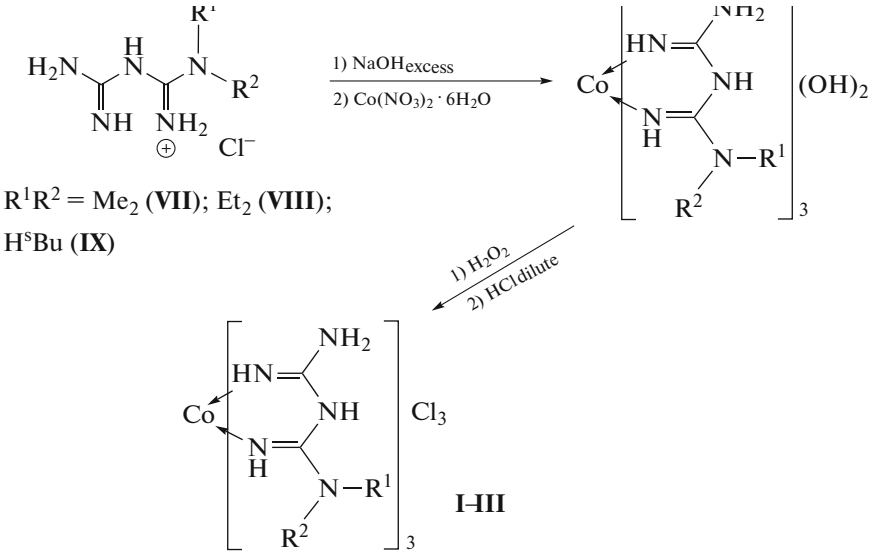
Table 3. Geometrical parameters of the hydrogen bonds in structure **III***

D–H···A	Distance, Å			Angle DHA, deg
	D–H	H···A	D···A	
O(1*w*)–H(1*wA*)···Cl(1)	0.89(2)	2.57(14)	3.301(4)	140(18)
O(1*w*)–H(1*wB*)···Cl(2)	0.89(2)	2.34(8)	3.195(5)	160(18)
O(2*w*)–H(2*wA*)···Cl(3)	0.90(2)	2.50(2)	3.152(5)	129(3)
O(2*w*)–H(2*wB*)···Cl(4)	0.91(2)	2.21(2)	3.057(6)	155(6)
N(21)–H(21)···O(1*w*)$^{\#1}$	0.88	2.31	3.172(5)	165.0
N(31)–H(31)···O(1*w*)	0.88	2.36	3.199(5)	159.3
N(23)–H(23)···O(2*w*)$^{\#2}$	0.88	2.17	2.915(7)	142.8
N(24)–H(24)···O(2*w*)$^{\#2}$	0.88	2.06	2.863(7)	151.4
N(13)–H(13)···Cl(1)$^{\#1}$	0.88	2.56	3.376(5)	154.8
N(22)–H(22)···Cl(1)	0.88	2.60	3.363(4)	145.5
N(25)–H(25*D*)···Cl(1)	0.88	2.63	3.385(6)	144.4
N(33)–H(33)···Cl(1)$^{\#3}$	0.88	2.52	3.344(5)	157.1
N(34)–H(34)···Cl(1)$^{\#3}$	0.88	2.42	3.165(4)	142.1
N(15)–H(15*D*)···Cl(2)	0.88	2.40	3.229(5)	158.1
N(32)–H(32)···Cl(2)$^{\#1}$	0.88	2.61	3.330(4)	139.5
N(35)–H(35*D*)···Cl(2)$^{\#1}$	0.88	2.53	3.266(5)	142.2
N(14)–H(14)···Cl(3)$^{\#4}$	0.88	2.44	3.262(4)	154.6
N(15)–H(15*E*)···Cl(3)$^{\#4}$	0.88	2.34	3.182(5)	159.9
N(25)–H(25*E*)···Cl(3)$^{\#2}$	0.88	2.54	3.318(5)	147.7

* The symmetry operations are $^{\#1}$ $1 + x, y, z$; $^{\#2}$ $1 - x, y - 1/2, 2 - z$; $^{\#3}$ $1 + x, y, 1 + z$; $^{\#4}$ $x, y, z - 1$.

RESULTS AND DISCUSSION

Complexes **I**–**III** were obtained as described for the synthesis of the complex $[Co(NH_2C(=NH)NHC(=NH)NH_2)_3]Cl_3$ with unsubstituted biguanide [14] as follows:



R^{1}R^2 = Me_2 (**VII**); Et_2 (**VIII**); H^{s}Bu (**IX**)

Scheme 1.

Table 4. Antiviral activity characteristics

Complex	CD_{50}, μg/mL	ID_{50}, μg/mL	IS
I	>1000	Not reached	
II	250	250	1
III	1000	125	8
IV	1000	120	8.3
V	1000	250	4
VI	>1000	Not reached	

The exception was that H_2O_2 rather than air was used as an oxidant in the second step. This reduced the reaction time and increased the yields of the complexes.

Structure **III** contains the single crystallographically independent complex cation $[Co(NH_2C(NH)NHC(NH)NH^sBu)_3]^{3+}$. The Co atom is coordinated by six imine N atoms of three chelating ^{s}Bu-biguanide ligands that make up a nearly perfect octahedron (Fig. 1). The Co–N bond lengths are 1.911(4)–1.921(4) Å; the NCoN *cis*- and *trans*-angles are 88.64(17)°–91.75(18)° and 177.4(2)°–178.5(2)°, respectively (Table 2). The ^{s}Bu substituents are in the *mer*-configuration. One of the three six-membered chelate rings Co(1)N(11)C(11)N(14)C(13)N(12) is nearly planar (±0.08 Å), while the two other rings adopt a boat conformation. The Co atoms and the N atoms of the central NH groups lie above the C_2N_2 plane; their deviations are 0.455 and 0.443 Å for Co and 0.186 and 0.198 Å for N. The C=N bonds (1.276(7)–1.288(6) Å) are appreciably shorter than the other N–C bonds (1.378(6)–1.394(6) Å for the central N atom and 1.318(7)–1.354(6) Å for the terminal N atoms), which suggests considerable conjugation over the fragment N_5C_2.

The anionic part of structure **III** consists of three crystallographically independent chloride ions forming a network of hydrogen bonds O–H···Cl and N–H···Cl involving the H atoms of crystal water molecules and the ^{s}Bu-biguanide ligands of the complex cations (Fig. 2). These hydrogen bonds, along with N–H···O, give rise to a 3D framework motif (the shortest distances: O···Cl, ~3.06 Å, N···O, ~2.86 Å, and N···Cl, ~3.16 Å) (Table 3).

The data from IR and UV-Vis spectroscopy and elemental analysis (Table 5) agree with the molecular structure determined by X-ray diffraction. The IR spectrum of complex **III** shows the same characteristic vibrations as in the spectrum of the starting biguanide hydrochloride **IX** (NH stretching and bending vibrations, C=N stretching vibrations). The coordination of biguanide to the Co atom shifts the ν(NH) and

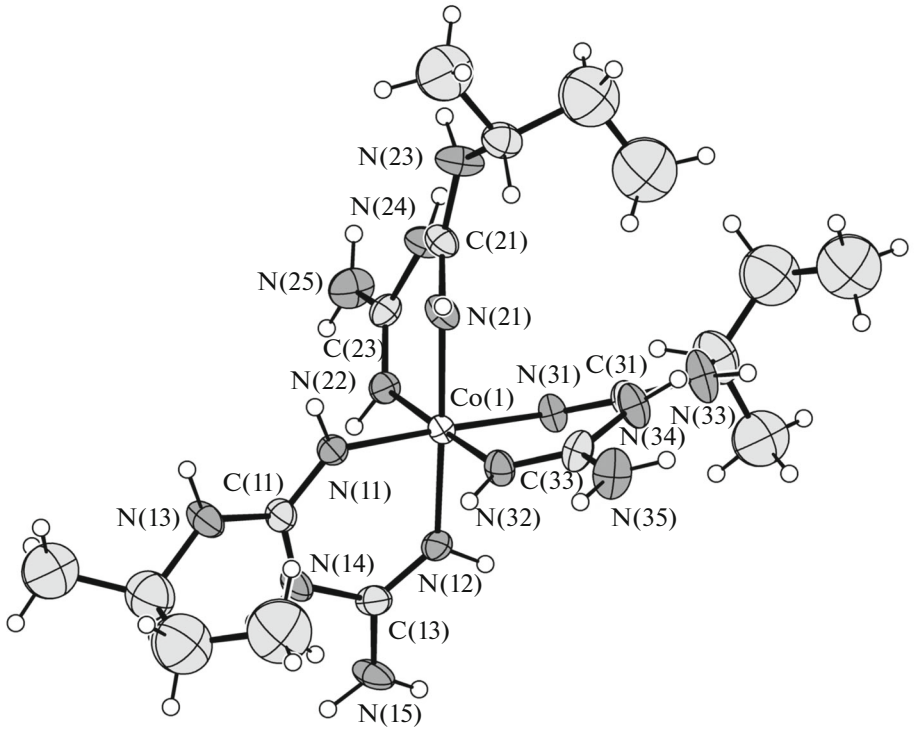


Fig. 1. Complex cation in structure **III** with atomic displacement ellipsoids (50% probability).

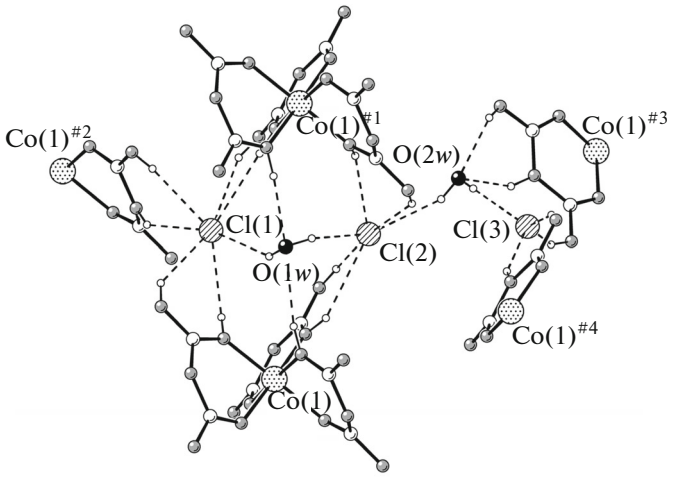


Fig. 2. Hydrogen bonds in structure **III**. The alkyl substituents of the biguanide ligands and the H atoms not involved in hydrogen bonding are omitted. The symmetry operations are $^{\#1}$ $x-1, y, z$; $^{\#2}$ $x-1, y, z-1$; $^{\#3}$ $1-x, 1/2+y, 2-z$; $^{\#4}$ $x, y, 1+z$.

ν(C=N) bands to the higher frequencies by ~40 cm^{-1} (from 1640 to 1679 cm^{-1}); the positions of the δ(NCN) and δ(CNH) bands change only slightly. The electronic absorption spectrum shows four bands with λ_{max} = 480 (ε = 134), 353 (ε = 160), and 275 nm (ε = 300). This set of bands is characteristic of low-spin octahedral Co(III) complexes with nitrogen-containing ligands [15]. The spectral parameters of complexes **I** and **II** are similar to those of complex **III**.

Unlike their precursors $[Co(NH_2C(=NH)NHC(=NH)NR^1R^2)_3](OH)_2$ (R^1R^2 = Me_2 (**VII**), Et_2 (**VIII**), and H^sBu (**IX**)), complexes **I**–**III** containing outer-sphere chloride anions are well soluble in water and stable at pH values of biological systems, e.g., the culture media MEM and DMEM used subsequently for studying the in vitro cytotoxic and antiviral activity of the test complexes.

Complexes **I**–**III** and complexes **IV**–**VI** (obtained earlier) were tested for antiviral activity [18]. Complex **VI** with ethylenediamine was used because it is the simplest chelate Co(III) complex containing no free functional groups. Complex **III** and both thiourea complexes are promising for further antiviral activity testing. These complexes have very low toxicity and show the highest antiviral activity and therapeutic efficacy among all the samples tested. These encouraging results provide a basis for further investigations of Co(III) biguanide complexes as antiviral drugs.

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Table 5. IR and UV-Vis spectra and elemental analysis data

	IR ν, cm^{-1} (KBr)	UV-Vis λ, nm (ε)	Elemental analysis	
			found	calculated
I	3321. 3182. 3036 ν(NH) + ν(OH); 2822 ν(CH); 1681 ν(N=C); 1646 δ(NCN); 1507, 1448 δ(CNH)	275 (316), 354 (180), 478 (153)	N, 37.0; C, 25.1; H, 6.3; Cl, 18.4	$C_{12}H_{35}N_{15}OCl_3Co$ N, 36.81; C, 25.25; H, 6.18; Cl, 18.63
II	3390, 3306, 3192 ν(NH); 2979, 2933 ν(CH); 1679 ν(N=C); 1633 δ(NCN); 1501, 1385 δ(CNH)	280 (349), 354 (150), 478 (128)	N, 28.1; C, 36.2; H, 7.7; Cl, 17.7	$C_{18}H_{45}N_{15}Cl_3Co$ N, 28.32; C, 36.41; H, 7.64; Cl, 17.68
III	3462 ν(OH); 3301, 3266, 3176, 3124 ν(NH) + ν(OH); 2969, 2931, 2879 ν(CH); 1679 ν(N=C); 1558 δ(NCN); 1465, 1361 δ(CNH)	275 (300), 353 (160), 480 (133)	H, 7.3; C, 35.2; N, 27.4; Cl, 17.3	$C_{18}H_{49}N_{15}O_2Cl_3Co$ N, 27.22; C, 34.99; H, 7.34; Cl, 16.99
VII	3382, 3308, 3172, 3010 ν(NH); 2822 ν(CH); 1651 ν(N=C); 1573 δ(NCN); 1484, 1418 δ(CNH)			
VIII	3392, 3323, 3198 ν(NH); 2981, 2941 ν(CH); 1634 ν(N=C); 1561 δ(NCN); 1495, 1382 δ(CNH)			
IX	3362, 3317, 3202, 3140 ν(NH); 2970, 2945, 2877 ν(CH); 1640 ν(N=C); 1573 δ(NCN); 1544, 1481 δ(CNH)			

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