



Syntheses, crystal structures and properties of copper(II) complexes of 1-amidinoisourea and biguanide nitrates

Zdeněk Jalový^{a,*}, Zdeňka Padělková^b, Robert Jirásko^c, Robert Matyáš^a, Michal Holčapek^c, Ondřej Němec^a, Miroslava Novotná^d, Linda Mišková^d

^a University of Pardubice, Faculty of Chemical Technology, Institute of Energetic Materials, Studentská 95, CZ-532 10 Pardubice, Czech Republic

^b University of Pardubice, Faculty of Chemical Technology, Department of General and Inorganic Chemistry, Studentská 95, CZ-532 10 Pardubice, Czech Republic

^c University of Pardubice, Faculty of Chemical Technology, Department of Analytical Chemistry, Studentská 95, CZ-532 10 Pardubice, Czech Republic

^d Institute of Chemical Technology Prague, Laboratory of Molecular Spectroscopy, Technická 5, CZ-166 28 Prague 6, Czech Republic

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ABSTRACT

Copper(II) complexes of amidinoisourea and biguanidine derivatives $[\text{Cu}\{\text{NH}_2(\text{C}=\text{NH})\text{NH}(\text{C}=\text{NH})\text{Y}\}_2(\text{NO}_3)_2]$, where $\text{Y} = \text{OR}, \text{NHR}$ or NRR ($\text{R} = \text{Me}, \text{Et}, \text{Pr}, \text{iPr}, \text{allyl}, \text{Bu}, \text{iBu}, \text{Bz}, \text{Cp}, \text{Cy}$) suitable for inflating gas generating systems were synthesized and characterized by elemental analysis, mass spectrometry and FTIR spectroscopy. The structures of three complexes were determined by X-ray diffraction. Thermal behavior was studied by differential thermal analysis and the decomposition temperatures indicated good thermal stability. Enthalpies of formation of the complexes are influenced by the substituent Y .

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1. Introduction

1-Amidinoisourea and biguanide metal complex compounds were described more than a hundred years ago, often without their structures being known [1]. More recently, Diana et al. [2] disproved the idea that 1-amidino-2-alkylisoureas rearrange to 1-amidino-3-alkylureas and stated that the ligands in the complexes are solely 1-amidino-2-alkylisoureas. Biguanide metal complexes or their ligands have been described for various applications in medicinal chemistry [3,4].

Recently, we have tested these compounds as part of pyrotechnic compositions for inflating automobile safety systems, namely airbags and seatbelt pre-tensioners [5–7]. The main reason for this is to replace sodium azide and double base propellants (based on nitrocellulose) in gas generating mixtures. Although sodium azide has excellent properties for such purposes, since it is easily available and the pyrotechnic composition during safety system deployment produces no toxic nitrogen and a low content of other toxic gases [8–10]. On the other hand, the use of sodium azide causes problems from many aspects: it is itself highly toxic, in neutral or acidic solutions it releases the very poisonous and volatile hydrazoic acid, it is a broad-spectrum biocide with an as yet

unknown environmental fate and thus it has been criticized from many points of view [11–13]. Also, sodium azide, as a major part of safety pyrotechnics devices, causes problems during recycling of vehicles and the handling of highly toxic waste. As for double base propellants, based on nitrocellulose, they are excellent propellants [14,15], but long-term stability and toxic gaseous products (containing nitrogen oxides and carbon monoxide) limit its application in recent years.

Many organic compounds, such as derivatives of furazane [16,17], guanidine [18] or tetrazole [19–21] may form a part of the pyrotechnics mixture for these purposes. However, the production cost, the multi-step synthesis processes, unstable intermediates or long-term instability are limiting factors for the use of such compounds.

Our first idea was to use bis(cyanoguanidine)copper(II) nitrate (**1**, Fig. 1), but this has a low decomposition temperature and low chemical stability. Therefore, we looked at those addition products of alcohols and amines to **1** that give complexes of 1-amidinoisourea (**2–8**) and biguanides (**9–17**) which have higher decomposition temperatures and better chemical stability than **1**. The materials were used as part of the mixture together with oxidisers and binders. Copper in the complexes serves as a combustion catalyst [22,23].

The aim of the study was to prepare the complex compounds, prove their structure, determine their enthalpies of formation

* Corresponding author.

E-mail address: zdenek.jalovy@upce.cz (Z. Jalový).

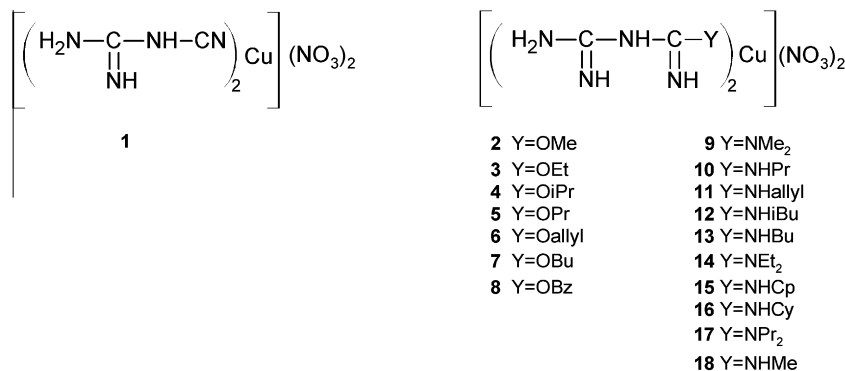


Fig. 1. List of complex compounds studied.

and estimate the decomposition temperatures. The last two characteristics are the important crucial properties for their use in inflating safety systems.

2. Experimental

2.1. General procedures

Positive-ion and negative-ion electrospray ionization (ESI) mass spectra were measured on an ion trap analyzer (Esquire 3000, Bruker Daltonics, Germany). The full scan mass spectra were measured in the range m/z 50–1000. The samples were dissolved in a water/acetonitrile (1:1) mixture and analyzed by direct infusion at a flow rate of $5 \mu\text{l min}^{-1}$. The ion source temperature was 300°C , the flow rate and the nitrogen pressure nitrogen were 4 l min^{-1} and 10 psi, respectively. All masses listed in this section are related to the monoisotopic elemental composition. FTIR spectra were collected using a NICOLET 6700 FTIR spectrometer with the diamond ATR accessory GladiATR (PIKE Electronics). A powder sample of each complex was measured without any adjustment. The FTIR spectrum of the compound was recorded in the spectral range $4000\text{--}400 \text{ cm}^{-1}$, the spectrometer had a spectral resolution of 4 cm^{-1} and 64 scans. Spectral manipulation was made using the multi-tasking software OMNIC v. 7.3. Heat of combustion was measured using an MS-10A combustion calorimeter (Laget) in an oxygen atmosphere (oxygen pressure was 2 MPa, sample mass was approx. 0.6 g). The calorimeter was calibrated using benzoic acid (heat of combustion 26434 J g^{-1}). The thermal analysis was studied using a differential thermal analyzer DTA 550Ex (OZM Research). The 50 mg samples were tested in open glass microtest tubes (in contact with air) and the heating rate was 5°C min^{-1} . The melting points were measured on a Kofler bench and are uncorrected. If no melting occurred before reaching 360°C , it is mentioned as $>360^\circ\text{C}$.

2.2. Preparation of bis(cyanoguanidine)copper(II) nitrate (**1**)

Copper nitrate trihydrate (8.00 g, 33.1 mmol) in ethyl acetate (600 ml) was added to a boiling solution of cyanoguanidine (5.6 g, 66.6 mmol) in ethyl acetate (1600 ml) over 30 min. Heating under reflux was continued for an additional 2 h. After cooling to room temperature, the product was filtered and washed with fresh ethyl acetate to give 11.47 g (97%) of a bright green solid; m.p. $>360^\circ\text{C}$. The product was stored in a desiccator under phosphorous pentoxide. *Anal.* Calc. for $\text{C}_4\text{H}_8\text{CuN}_{10}\text{O}_6$ (355.75): C, 13.50; H, 2.27; Cu, 17.86; N, 39.37. Found: C, 13.93; H, 2.58; Cu, 17.56; N, 39.14%. Positive ion ESI-MS: m/z 231 $[\text{M}-2\text{NO}_3]^+$, 100%; m/z 189 $[\text{M}-2\text{NO}_3-\text{CH}_2\text{N}_2]^+$; m/z 165 $[\text{M}-2\text{NO}_3-2\text{CH}_2\text{N}_2+\text{H}_2\text{O}]^+$. FTIR (cm^{-1}): 3448 $\nu(\text{NH})$; 3330 $\nu_{\text{as}}(\text{NH}_2)$; 3274 $\nu(\text{NH})$; 3172

$\nu_{\text{s}}(\text{NH}_2)$; 2246 $\nu(\text{C}\equiv\text{N})$; 2197 $\nu(\text{C}\equiv\text{N})$; 1668, 1649 $\nu(\text{C}=\text{N})$; 1548 $\nu(\text{C}=\text{N})$ in chelate ring; 1507 $\nu(\text{C}=\text{N})$ in chelate ring, disloc. electron; 1377 $\nu(\text{NO}_3^-)$; 1340, 1247 δ chelate ring, 1112, 1056, 1028 $\nu(\text{C}-\text{N})$; 955, 930, 820, 728, 669 $\omega(\text{N}-\text{H})$; 566, 525, 509, 481 δ chelate ring; 566, 525, 509, 481 δ chelate ring.

2.3. Preparation of bis(1-amidino-2-substitutedisourea)copper(II) nitrates (**2–8**)

The complexes were prepared by the reaction of **1** with the corresponding alcohol (procedure A, Scheme 1) or by the reaction of copper nitrate trihydrate and cyanoguanidine in a 1:2 molar ratio and the corresponding alcohol (procedure B, Scheme 2). Typical preparations are described as follows.

2.3.1. Bis(1-amidino-2-methylisourea)copper(II) nitrate (**2**)

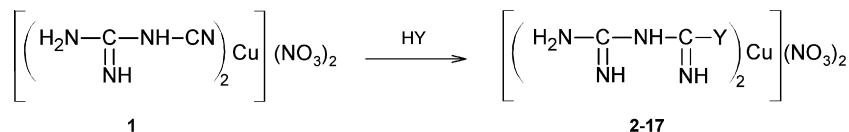
(A) Bis(cyanoguanidine)copper(II) nitrate (**1**, 0.65 g, 1.82 mmol) was dissolved in methanol (50 ml) and the solution was heated under reflux for 2 h. The resulting solid was filtered to give 0.73 g (95%) of the pink solid; m.p. $>360^\circ\text{C}$. *Anal.* Calc. for $\text{C}_6\text{H}_{16}\text{CuN}_{10}\text{O}_8$ (419.83): C, 17.17; H, 3.84; Cu, 15.14; N, 33.36. Found: C, 17.13; H, 3.80; Cu, 14.94; N, 33.43%. Positive ion ESI-MS: m/z 294 $[\text{M}-\text{HNO}_3-\text{NO}_3]^+$, 100%; m/z 252 $[\text{M}-\text{HNO}_3-\text{NO}_3-\text{CH}_2\text{N}_2]^+$; m/z 220 $[\text{M}-\text{HNO}_3-\text{NO}_3-\text{CH}_2\text{N}_2-\text{CH}_3\text{OH}]^+$. Negative ion ESI-MS: m/z 418 $[\text{M}-\text{H}]^-$, 100%; m/z 355 $[\text{M}-\text{H}-\text{HNO}_3]^-$.

(B) Copper nitrate trihydrate (5.00 g, 20.8 mmol) in methanol (20 ml) was added to a boiling solution of cyanoguanidine (3.50 g, 41.6 mmol) in methanol (120 ml) over 45 min. The color of the reaction mixture turned from bright green to blue and towards the end of the addition started to turn dark blue and finally pink. Heating under reflux was continued for an additional 4 h. After cooling to room temperature the product was filtered and washed with fresh methanol to give 8.57 g (99%) of a pink solid. m.p. $>360^\circ\text{C}$. *Anal.* Calc. for $\text{C}_6\text{H}_{16}\text{CuN}_{10}\text{O}_8$ (419.83): C, 17.17; H, 3.84; Cu, 15.14; N, 33.36. Found: C, 17.11; H, 3.80; Cu, 14.99; N, 33.32%.

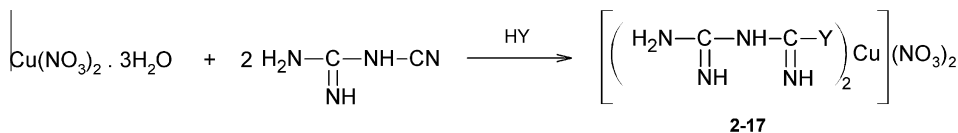
2.3.2. Bis(1-amidino-2-ethylisourea)copper(II) nitrate (**3**)

(A) Yield 97%; m.p. $>360^\circ\text{C}$. *Anal.* Calc. for $\text{C}_8\text{H}_{20}\text{CuN}_{10}\text{O}_8$ (447.89): C, 21.45; H, 4.50; Cu, 14.19; N, 31.27. Found: C, 21.50; H, 4.58; Cu, 14.03; N, 31.21%. Positive ion ESI-MS: m/z 322 $[\text{M}-\text{HNO}_3-\text{NO}_3]^+$, 100%; m/z 280 $[\text{M}-\text{HNO}_3-\text{NO}_3-\text{CH}_2\text{N}_2]^+$; m/z 234 $[\text{M}-\text{HNO}_3-\text{NO}_3-\text{CH}_2\text{N}_2-\text{C}_2\text{H}_5\text{OH}]^+$. Negative ion ESI-MS: m/z 446 $[\text{M}-\text{H}]^-$, 100%; m/z 383 $[\text{M}-\text{H}-\text{HNO}_3]^-$; m/z 125 $[(\text{HNO}_3)_2-\text{H}]^-$; m/z 62 $[\text{NO}_3]^-$.

(B) Yield 98%; m.p. $>360^\circ\text{C}$. *Anal.* Calc. for $\text{C}_8\text{H}_{20}\text{CuN}_{10}\text{O}_8$ (447.89): C, 21.45; H, 4.50; Cu, 14.19; N, 31.27. Found: C, 21.47; H, 4.59; Cu, 14.01; N, 31.18%.



Scheme 1. Preparation of **2-17** by reaction of **1** with the corresponding amine.



Scheme 2. Preparation of **9-17** by reaction of copper nitrate trihydrate, cyanoguanidine and the corresponding amine.

2.3.3. Bis(1-amidino-2-isopropylisourea)copper(II) nitrate (**4**)

(A) –

(B) Yield 99%; m.p. > 360 °C. *Anal. Calc.* for $\text{C}_{10}\text{H}_{24}\text{CuN}_{10}\text{O}_8$ (475.94): C, 25.24; H, 5.08; Cu, 13.35; N, 29.43. Found: C, 24.99; H, 4.81; Cu, 13.81; N, 29.41%. Positive ion ESI-MS: m/z 350 $[\text{M}-\text{HNO}_3-\text{NO}_3]^+$, 100%; m/z 308 $[\text{M}-\text{HNO}_3-\text{NO}_3-\text{CH}_2\text{N}_2]^+$; m/z 265 $[\text{M}-\text{HNO}_3-\text{NO}_3-\text{CH}_2\text{N}_2-\text{C}_3\text{H}_7]^+$. Negative ion ESI-MS: m/z 474 $[\text{M}-\text{H}]^-$, 100%; m/z 411 $[\text{M}-\text{H}-\text{HNO}_3]^-$; m/z 125 $[(\text{HNO}_3)_2-\text{H}]^-$; m/z 62 $[\text{NO}_3]^-$.

The crystals suitable for X-ray analysis were prepared by dissolving **1** in isopropylalcohol and allowing to stand at room temperature for several days.

2.3.4. Bis(1-amidino-2-propylisourea)copper(II) nitrate (**5**)

(A) –

(B) Yield 99%; m.p. > 360 °C. *Anal. Calc.* for $\text{C}_{10}\text{H}_{24}\text{CuN}_{10}\text{O}_8$ (475.94): C, 25.24; H, 5.08; Cu, 13.35; N, 29.43. Found: C, 25.32; H, 5.13; Cu, 13.05; N, 29.60%. Positive ion ESI-MS: m/z 350 $[\text{M}-\text{HNO}_3-\text{NO}_3]^+$, 100%; m/z 308 $[\text{M}-\text{HNO}_3-\text{NO}_3-\text{CH}_2\text{N}_2]^+$; m/z 265 $[\text{M}-\text{HNO}_3-\text{NO}_3-\text{CH}_2\text{N}_2-\text{C}_3\text{H}_7]^+$. Negative ion ESI-MS: m/z 474 $[\text{M}-\text{H}]^-$, 100%; m/z 411 $[\text{M}-\text{H}-\text{HNO}_3]^-$; m/z 125 $[(\text{HNO}_3)_2-\text{H}]^-$; m/z 62 $[\text{NO}_3]^-$.

2.3.5. Bis(1-amidino-2-allylisourea)copper(II) nitrate (**6**)

(A) Yield 83%; m.p. 184–186 °C. *Anal. Calc.* for $\text{C}_{10}\text{H}_{20}\text{CuN}_{10}\text{O}_8$ (471.91): C, 25.45; H, 4.27; Cu, 13.47; N, 29.68. Found: C, 17.13; H, 3.80; Cu, 14.94; N, 33.43%. Positive ion ESI-MS: m/z 346 $[\text{M}-\text{HNO}_3-\text{NO}_3]^+$, 100%; m/z 304 $[\text{M}-\text{HNO}_3-\text{NO}_3-\text{CH}_2\text{N}_2]^+$; m/z 263 $[\text{M}-\text{HNO}_3-\text{NO}_3-\text{CH}_2\text{N}_2-\text{allyl}]^+$. Negative ion ESI-MS: m/z 470 $[\text{M}-\text{H}]^-$; m/z 407 $[\text{M}-\text{H}-\text{HNO}_3]^-$, 100%; m/z 125 $[(\text{HNO}_3)_2-\text{H}]^-$; m/z 62 $[\text{NO}_3]^-$.

(B) –

2.3.6. Bis(1-amidino-2-butyliourea)copper(II) nitrate (**7**)

(A) –

(B) Yield 91%; m.p. > 360 °C. *Anal. Calc.* for $\text{C}_{12}\text{H}_{28}\text{CuN}_{10}\text{O}_8$ (503.99): C, 28.60; H, 5.60; Cu, 12.61; N, 27.79. Found: C, 28.32; H, 5.32; Cu, 12.26; N, 27.51%. Positive ion ESI-MS: m/z 378 $[\text{M}-\text{HNO}_3-\text{NO}_3]^+$, 100%; m/z 336 $[\text{M}-\text{HNO}_3-\text{NO}_3-\text{CH}_2\text{N}_2]^+$; m/z 279 $[\text{M}-\text{HNO}_3-\text{NO}_3-\text{CH}_2\text{N}_2-\text{C}_4\text{H}_9]^+$. Negative ion ESI-MS: m/z 502 $[\text{M}-\text{H}]^-$, 100%; m/z 439 $[\text{M}-\text{H}-\text{HNO}_3]^-$; m/z 125 $[(\text{HNO}_3)_2-\text{H}]^-$; m/z 62 $[\text{NO}_3]^-$.

2.3.7. Bis(1-amidino-2-benzylisourea)copper(II) nitrate (**8**)

(A) –

(B) Larger amount of benzylalcohol than in general procedure 2.3.1.B was used in order to dissolve starting materials. Yield 82%; m.p. 162–167 °C. *Anal. Calc.* for $\text{C}_{18}\text{H}_{24}\text{CuN}_{10}\text{O}_8$ (572.02): C, 37.80; H, 4.23; Cu, 11.11; N, 22.38. Found: C, 38.22; H, 4.20; Cu, 11.11; N, 22.70. Positive ion ESI-MS: m/z 446 $[\text{M}-\text{HNO}_3-\text{NO}_3]^+$, 100%;

m/z 404 $[\text{M}-\text{HNO}_3-\text{NO}_3-\text{CH}_2\text{N}_2]^+$; m/z 313 $[\text{M}-\text{HNO}_3-\text{NO}_3-\text{CH}_2\text{N}_2-\text{C}_7\text{H}_7]^+$. Negative ion ESI-MS: m/z 570 $[\text{M}-\text{H}]^-$, 100%; m/z 507 $[\text{M}-\text{H}-\text{HNO}_3]^-$; m/z 125 $[(\text{HNO}_3)_2-\text{H}]^-$; m/z 62 $[\text{NO}_3]^-$.

2.4. Preparation of bis(1-substitutedbiguanide)copper(II) nitrates (**9-17**)

Bis(1-substitutedbiguanide)copper(II) nitrates were prepared by the reaction of **1** with the corresponding amine (procedure A, [Scheme 1](#)) or by the reaction of copper nitrate trihydrate and cyanoguanidine in a 1:2 molar ratio and the corresponding amine (procedure B, [Scheme 2](#)) and, only in the case of **9**, by reaction of copper nitrate trihydrate with the molecule that forms the ligand (procedure C). Typical preparations are described in Sections 2.4.1 and 2.4.2.

2.4.1. Bis(1,1-dimethylbiguanide)copper(II) nitrate (**9**)

(A) Bis(cyanoguanidine)copper(II) nitrate (**1**, 2.00 g, 5.62 mmol) was dissolved in dimethylamine (50 ml) and the solution was heated under reflux for 2 h. The amine was evaporated *in vacuo* and the residue was treated with ethanol (20 ml). The solid was filtered and washed with fresh ethanol to give 2.25 g (90%) of a pink solid; m.p. > 360 °C. *Anal. Calc.* for $\text{C}_8\text{H}_{22}\text{CuN}_{12}\text{O}_6$ (445.92): C, 21.55; H, 4.97; Cu, 14.25; N, 37.69. Found: C, 21.94; H, 5.15; Cu, 14.29; N, 37.73%. Positive ion ESI-MS: m/z 320 $[\text{M}-\text{HNO}_3-\text{NO}_3]^+$; m/z 278 $[\text{M}-\text{HNO}_3-\text{NO}_3-\text{CH}_2\text{N}_2]^+$; m/z 130 $[\text{L}+\text{H}]^+$, 100%; m/z 88 $[\text{L}+\text{H}-\text{CH}_2\text{N}_2]^+$. Negative ion ESI-MS: m/z 507 $[\text{M}+\text{NO}_3]^-$; m/z 446 $[\text{M}-\text{H}+\text{H}_2]^-$; m/z 444 $[\text{M}-\text{H}]^-$; m/z 254 $[\text{L}+\text{NO}_3+\text{HNO}_3]^-$, 100%; m/z 125 $[(\text{HNO}_3)_2-\text{H}]^-$; m/z 62 $[\text{NO}_3]^-$.

(B) –

(C) A solution of copper nitrate trihydrate (0.93 g, 3.85 mol) in methanol (30 ml) was added to a boiling solution of 1,1-dimethylbiguanide [[24](#)] (0.50 g, 3.87 mmol) in methanol (100 ml) over 30 min. The mixture was heated under reflux for an additional 3 h. After cooling to room temperature, the product was filtered and washed with fresh methanol to give 0.50 g (29%) of a pink solid; m.p. > 360 °C. *Anal. Calc.* for $\text{C}_8\text{H}_{22}\text{CuN}_{12}\text{O}_6$ (445.92): C, 21.55; H, 4.97; Cu, 14.25; N, 37.69. Found: C, 22.26; H, 5.20; Cu, 14.32; N, 37.49%.

2.4.2. Bis(1-propylbiguanide)copper(II) nitrate (**10**)

(A) Bis(cyanoguanidine)copper(II) nitrate (**1**, 2.00 g, 5.62 mmol) was dissolved in propylamine (50 ml) and the solution was heated under reflux for 2 h. The amine was evaporated *in vacuo* and the residue was treated with ethanol (20 ml). The solid was filtered and washed with fresh ethanol to give 1.28 g (48%) of a pink solid; m.p. > 360 °C. *Anal. Calc.* for $\text{C}_{10}\text{H}_{26}\text{CuN}_{12}\text{O}_6$ (473.96): C, 25.34; H, 5.53; Cu, 13.41; N, 35.46. Found: C, 26.11; H, 5.49; Cu, 12.96; N, 35.31%. Positive ion ESI-MS: m/z 348 $[\text{M}-\text{HNO}_3-\text{NO}_3]^+$, 100%; m/z 306 $[\text{M}-\text{HNO}_3-\text{NO}_3-\text{CH}_2\text{N}_2]^+$; m/z 264 $[\text{M}-\text{HNO}_3-\text{NO}_3-\text{CH}_2$

$\text{N}_2\text{--C}_3\text{H}_6]^+$; m/z 206 $[\text{M--HNO}_3\text{--NO}_3\text{--2CH}_2\text{N}_2\text{--C}_3\text{H}_7\text{NH}]^+$; m/z 144 $[\text{L+H}]^+$. Negative ion ESI-MS: m/z 535 $[\text{M+NO}_3]^-$; m/z 472 $[\text{M--H}]^-$, 100%; m/z 125 $[(\text{HNO}_3)_2\text{--H}]^-$; m/z 62 $[\text{NO}_3]^-$.

(B) Copper nitrate trihydrate (5.00 g, 20.8 mmol) in propylamine (60 ml) was added to a solution of cyanoguanidine (3.5 g, 41.6 mmol) in propylamine (150 ml) over 60 min. Heating under reflux was continued for an additional 2 h. The amine was evaporated *in vacuo* and the residue was treated with ethanol (30 ml). The solid was filtered and washed with fresh ethanol to give 6.2 g (63%) of a pink solid; m.p. > 360 °C. *Anal. Calc.* for $\text{C}_{10}\text{H}_{26}\text{Cu--N}_{12}\text{O}_6$ (473.96): C, 25.34; H, 5.53; Cu, 13.41; N, 35.46. Found: C, 26.12; H, 5.51; Cu, 12.86; N, 34.49%.

2.4.3. Bis(1-allylbisguanide)copper(II) nitrate (**11**)

(A) –

(B) Yield 51%; m.p. > 360 °C. *Anal. Calc.* for $\text{C}_{10}\text{H}_{22}\text{CuN}_{12}\text{O}_6$ (469.94): C, 25.56; H, 4.72; Cu, 13.52; N, 35.77. Found: C, 25.77; H, 4.61; Cu, 13.08; N, 35.50%. Positive ion ESI-MS: m/z 344 $[\text{M--HNO}_3\text{--NO}_3]^+$, 100%; m/z 302 $[\text{M--HNO}_3\text{--NO}_3\text{--CH}_2\text{N}_2]^+$; m/z 262 $[\text{M--HNO}_3\text{--NO}_3\text{--CH}_2\text{N}_2\text{--C}_3\text{H}_4]^+$; m/z 204 $[\text{M--HNO}_3\text{--NO}_3\text{--2CH}_2\text{N}_2\text{--C}_3\text{H}_5\text{NH}]^+$; m/z 142 $[\text{L+H}]^+$. Negative ion ESI-MS: m/z 531 $[\text{M+NO}_3]^-$; m/z 468 $[\text{M--H}]^-$, 100%; m/z 62 $[\text{NO}_3]^-$.

2.4.4. Bis(1-isobutylbisguanide)copper(II) nitrate (**12**)

(A) –

(B) Yield 75%; m.p. 281–282 °C. *Anal. Calc.* for $\text{C}_{12}\text{H}_{30}\text{CuN}_{12}\text{O}_6$ (502.03): C, 28.71; H, 6.02; Cu, 12.66; N, 33.48. Found: C, 29.01; H, 5.79; Cu, 12.09; N, 33.34%. Positive ion ESI-MS: m/z 376 $[\text{M--HNO}_3\text{--NO}_3]^+$, 100%; m/z 334 $[\text{M--HNO}_3\text{--NO}_3\text{--CH}_2\text{N}_2]^+$; m/z 278 $[\text{M--HNO}_3\text{--NO}_3\text{--CH}_2\text{N}_2\text{--C}_4\text{H}_8]^+$; m/z 220 $[\text{M--HNO}_3\text{--NO}_3\text{--2CH}_2\text{N}_2\text{--C}_4\text{H}_9\text{NH}]^+$; m/z 158 $[\text{L+H}]^+$; m/z 116 $[\text{L+H--CH}_2\text{N}_2]^+$. Negative ion ESI-MS: m/z 563 $[\text{M+NO}_3]^-$; m/z 500 $[\text{M--H}]^-$, 100%.

2.4.5. Bis(1-butylbisguanide)copper(II) nitrate (**13**)

(A) –

(B) Yield 75%; m.p. 283–285 °C. *Anal. Calc.* for $\text{C}_{12}\text{H}_{30}\text{CuN}_{12}\text{O}_6$ (502.03): C, 28.71; H, 6.02; Cu, 12.66; N, 33.48. Found: C, 29.39; H, 6.12; Cu, 12.52; N, 32.85%. Positive ion ESI-MS: m/z 376 $[\text{M--HNO}_3\text{--NO}_3]^+$, 100%; m/z 334 $[\text{M--HNO}_3\text{--NO}_3\text{--CH}_2\text{N}_2]^+$; m/z 278 $[\text{M--HNO}_3\text{--NO}_3\text{--CH}_2\text{N}_2\text{--C}_4\text{H}_8]^+$; m/z 220 $[\text{M--HNO}_3\text{--NO}_3\text{--2CH}_2\text{N}_2\text{--C}_4\text{H}_9\text{NH}]^+$; m/z 158 $[\text{L+H}]^+$; m/z 116 $[\text{L+H--CH}_2\text{N}_2]^+$. Negative ion ESI-MS: m/z 563 $[\text{M+NO}_3]^-$; m/z 500 $[\text{M--H}]^-$, 100%; m/z 125 $[(\text{HNO}_3)_2\text{--H}]^-$; m/z 62 $[\text{NO}_3]^-$.

The crystals suitable for X-ray analysis were prepared by slow evaporation of the solvent (butylamine/methanol/ethyl acetate).

2.4.6. Bis(1,1-diethylbisguanide)copper(II) nitrate (**14**)

(A) –

(B) Yield 73%; m.p. 238–241 °C. *Anal. Calc.* for $\text{C}_{12}\text{H}_{30}\text{CuN}_{12}\text{O}_6$ (502.03): C, 28.71; H, 6.02; Cu, 12.66; N, 33.48. Found: C, 29.18; H, 6.05; Cu, 12.42; N, 32.37%. Positive ion ESI-MS: m/z 376 $[\text{M--HNO}_3\text{--NO}_3]^+$; m/z 334 $[\text{M--HNO}_3\text{--NO}_3\text{--CH}_2\text{N}_2]^+$; m/z 278 $[\text{M--HNO}_3\text{--NO}_3\text{--CH}_2\text{N}_2\text{--C}_4\text{H}_8]^+$; m/z 220 $[\text{M--HNO}_3\text{--NO}_3\text{--2CH}_2\text{N}_2\text{--C}_4\text{H}_9\text{NH}]^+$; m/z 158 $[\text{L+H}]^+$, 100%; m/z 116 $[\text{L+H--CH}_2\text{N}_2]^+$. Negative ion ESI-MS: m/z 563 $[\text{M+NO}_3]^-$; m/z 500 $[\text{M--H}]^-$; m/z 282 $[\text{L+NO}_3\text{+HNO}_3]^-$, 100%; m/z 125 $[(\text{HNO}_3)_2\text{--H}]^-$; m/z 62 $[\text{NO}_3]^-$.

2.4.7. Bis(1-cyclopentylbisguanide)copper(II) nitrate (**15**)

(A) –

(B) Yield 63%; m.p. > 360 °C. *Anal. Calc.* for $\text{C}_{14}\text{H}_{30}\text{CuN}_{12}\text{O}_6$ (526.05): C, 31.97; H, 5.75; Cu, 12.08; N, 31.95. Found: C, 32.24; H, 5.52; Cu, 11.81; N, 31.15%. Positive ion ESI-MS: m/z 400 $[\text{M--HNO}_3\text{--NO}_3]^+$; m/z 358 $[\text{M--HNO}_3\text{--NO}_3\text{--CH}_2\text{N}_2]^+$; m/z 290 $[\text{M--HNO}_3\text{--NO}_3\text{--CH}_2\text{N}_2\text{--C}_5\text{H}_8]^+$; m/z 232 $[\text{M--HNO}_3\text{--NO}_3\text{--2CH}_2\text{N}_2\text{--C}_5\text{H}_9\text{NH}]^+$; m/z 200.6 $[\text{M--2NO}_3]^{2+}$; m/z 170 $[\text{L+H}]^+$, 100%; m/z 128 $[\text{L+H--CH}_2\text{N}_2]^+$. Negative ion ESI-MS: m/z 587 $[\text{M+NO}_3]^-$; m/z 524 $[\text{M--H}]^-$, 100%.

2.4.8. Bis(1-cyclohexylbisguanide)copper(II) nitrate (**16**)

(A) –

(B) Yield 73%; m.p. > 360 °C. *Anal. Calc.* for $\text{C}_{16}\text{H}_{34}\text{CuN}_{12}\text{O}_6$ (554.10): C, 34.68; H, 6.19; Cu, 11.47; N, 30.33. Found: C, 35.78; H, 6.14; Cu, 10.95; N, 29.64%. Positive ion ESI-MS: m/z 428 $[\text{M--HNO}_3\text{--NO}_3]^+$, 100%; m/z 386 $[\text{M--HNO}_3\text{--NO}_3\text{--CH}_2\text{N}_2]^+$; m/z 304 $[\text{M--HNO}_3\text{--NO}_3\text{--CH}_2\text{N}_2\text{--C}_6\text{H}_{10}]^+$; m/z 246 $[\text{M--HNO}_3\text{--NO}_3\text{--2CH}_2\text{N}_2\text{--C}_6\text{H}_{11}\text{NH}]^+$; m/z 214.6 $[\text{M--2NO}_3]^{2+}$; m/z 184 $[\text{L+H}]^+$; m/z 142 $[\text{L+H--CH}_2\text{N}_2]^+$. Negative ion ESI-MS: m/z 615 $[\text{M+NO}_3]^-$; m/z 552 $[\text{M--H}]^-$, 100%; m/z 489 $[\text{M--H--HNO}_3]^-$; m/z 125 $[(\text{HNO}_3)_2\text{--H}]^-$; m/z 62 $[\text{NO}_3]^-$.

2.4.9. Bis(1,1-dipropylbisguanide)copper(II) nitrate (**17**)

(A) Yield 64%; m.p. 232–236 °C. *Anal. Calc.* for $\text{C}_{16}\text{H}_{38}\text{CuN}_{12}\text{O}_6$ (558.13): C, 34.43; H, 6.68; Cu, 11.39; N, 30.12. Found: C, 35.31; H, 6.91; Cu, 11.05; N, 29.14%. Positive ion ESI-MS: m/z 432 $[\text{M--HNO}_3\text{--NO}_3]^+$; m/z 390 $[\text{M--HNO}_3\text{--NO}_3\text{--CH}_2\text{N}_2]^+$; m/z 186 $[\text{L+H}]^+$, 100%; m/z 144 $[\text{L+H--CH}_2\text{N}_2]^+$. Negative ion ESI-MS: m/z 619 $[\text{M+NO}_3]^-$; m/z 558 $[\text{M--H+H}_2]^-$; m/z 556 $[\text{M--H}]^-$; m/z 310 $[\text{L+NO}_3\text{+HNO}_3]^-$, 100%; m/z 125 $[(\text{HNO}_3)_2\text{--H}]^-$; m/z 62 $[\text{NO}_3]^-$.

(B) –

2.4.10. Attempt for preparation of bis(1-methylbisguanide)copper(II) nitrate (**18**), formation of bis(1-methylbisguanidinato)copper(II):methanol complex (**19**)

The attempted preparation of bis(1-methylbisguanide)copper(II) nitrate both by methods A and B in a 40% methylamine water solution resulted in a product the elemental analysis of which did not correspond to **18** and thus the product was not further analyzed. By crystallization of the expected **18** in methylamine/methanol yielded crystals suitable for X-ray analysis. According to X-ray analysis, the crystallized product was identified as bis(1-methylbisguanidinato)copper(II):methanol complex (**19**).

2.5. Crystallography of **4**, **13** and **19**

The X-ray data for single crystals of **4**, **13** and **19** were obtained at 150 K using an Oxford Cryostream low-temperature device on a Nonius KappaCCD diffractometer with Mo K α radiation ($\lambda = 0.71073$ Å), a graphite monochromator, and the ϕ and χ scan mode. Data reductions were performed with DENZO-SMN [25]. The absorption was corrected by integration methods [26]. Structures were solved by direct methods (SIR92) [27] and refined by full matrix least-square based on F^2 (SHELXL97) [28]. Hydrogen atoms were mostly localized in difference Fourier maps. However, to ensure uniformity of treatment of the crystals, all the hydrogens were included in calculated positions and treated as riding atoms and assigned temperature factors $U_{\text{iso}}(\text{H}) = 1.2 U_{\text{eq}}(\text{pivot atom})$ or $1.5 U_{\text{eq}}(\text{C})$ for the methyl H atoms, with N–H = 0.86 Å and C–H = 0.96 Å and 0.93 Å for methyl and aromatic H atoms, respectively. The *n*-butyl chains in **13** are disordered, hence they were split into two positions and treated isotropically [occupancy ratio 0.69(2):0.31(2)].

$R_{\text{int}} = \sum |F_o^2 - F_{o,\text{mean}}^2| / \sum F_o^2$, $\text{GOF} = [\sum (w(F_o^2 - F_c^2)^2) / (N_{\text{diff}} - N_{\text{param}})]^{1/2}$ for all data, $R(F) = \sum ||F_o| - |F_c|| / \sum |F_o|$ for observed data, $wR(F^2) = [\sum (w(F_o^2 - F_c^2)^2) / (\sum w(F_o^2)^2)]^{1/2}$ for all data.

The crystallographic data and structure refinement parameters for complexes **4**, **13** and **19** are given in Table 1.

3. Results and discussion

3.1. Synthesis, differential thermal analysis and enthalpies of formation

The synthesis of bis(cyanoguanidine)copper(II) nitrate (**1**) has been described in the literature using the reaction of copper nitrate and cyanoguanidine in ethanol [29] or propan-2-ol [30]. In our experiments, we were not able to prepare **1** by the reaction of copper nitrate and cyanoguanidine in ethanol even at 0 °C. The product isolated was bis(1-amidino-2-ethylisourea)copper(II) nitrate, which was first indicated by FTIR where no absorption of nitrile group was observed. So, our results are in agreement with those of Begley et al. [31]. To avoid the addition of alcohols to the active nitrile group of cyanoguanidine activated in complexes, we chose ethyl acetate as the solvent for the preparation of **1** using the reaction of copper nitrate trihydrate and cyanoguanidine. The yield of **1** was almost quantitative.

Complex **1** may be used as a starting material for the synthesis of copper(II) complexes with amidinoisoureas and biguanides as ligands. They are formed by heating **1** in the appropriate alcohol [30] or amine (Scheme 1). This method is mentioned as procedure A. The method is convenient in the laboratory, but inconvenient on a pilot-plant scale due to the large volume of ethyl acetate used for synthesizing **1** in order to dissolve the starting materials. Further search of the literature showed that copper complexes of amidinoisoureas have been synthesized by the reaction of the copper salt and cyanoguanidine in alcohol [30,32–36]. This procedure we used as a convenient method for preparation of bis(1-biguanide)copper(II) nitrates (**9–17**) using the reaction of copper nitrate trihydrate, cyanoguanidine and the corresponding amine (Scheme 2). In previously published methods, the ligands of corresponding biguanides were prepared and treated with the copper salt [32,37–39].

The results of all syntheses are summarized in Table 2. The yields of amidinoisoureas are almost quantitative in the case of

2–5. Yields of biguanides are lower due to the higher solubility of the complexes in the reaction media.

The thermal properties of the complexes were studied by differential thermal analysis (DTA). Start of decomposition is expressed as the beginning of the peak. The temperature at which maximum decomposition, as a characteristic value for individual compounds with exothermic decomposition, was also evaluated. The results are shown in Table 2. Bis(cyanoguanidine)copper(II) nitrate (**1**) starts decomposing at low temperatures. Most amidinoisoureas and biguanides have a higher decomposition temperature than **1**, and biguanides have a higher decomposition temperature than amidinoisoureas. It is seen when the 1-amidinoisourea complex is compared with the corresponding biguanide (e.g. **5** and **10**, **6** and **11** or **7** and **13**, see Table 2). Compounds **1** and **2** have a simple decomposition curve with no evidence of *endo*-process (Fig. 2). Most of amidinoisoureas and biguanides have a similar manner of decomposition: starting with *exo*-effect, followed by combination of *endo*- and *exo*-processes and finally terminated by the main *exo*-reaction. This is illustrated in Fig. 3 for selected amidinoisoureas and in Fig. 4 for selected biguanides.

The heats of combustion and enthalpies of formation are summarized in Table 3. The choice of substituent Y in complexes may influence both the carbon and nitrogen content and the enthalpies of formation. Complexes of biguanide generally have higher enthalpies of formation than 1-amidinoisoureas. In each group, the enthalpy of formation is influenced by substituent Y. Substituents with a double bond or cycles enhance the final enthalpy of the whole molecule. The higher heat of formation not accompanied by a lower decomposition temperature is excellent news for practical use in pyrotechnic compositions.

3.2. X-ray crystallography

All structures determined by X-ray crystallographic techniques reveal a high degree of planarity within the 1-amidinoisourea and biguanide [40–44] moieties where also the N–C bond distances

Table 1
Crystallographic data for compounds **4**, **13** and **19**.

Compound	4	13	19
Formula	C ₁₀ H ₂₄ CuN ₁₀ O ₈	C ₁₂ H ₃₀ CuN ₁₂ O ₆ ·2(CH ₃ OH)	C ₇ H ₂₀ CuN ₁₀ O
Formula weight	475.93	758.36	323.87
Crystal size (mm)	0.41 × 0.30 × 0.20	0.45 × 0.25 × 0.06	0.33 × 0.19 × 0.13
Crystal description	block	plate	plate
Crystal color	violet	pink	pink
Cell setting	monoclinic	monoclinic	monoclinic
Space group	P2 ₁ /c	C2/c	P2 ₁ /c
a (Å)	15.3330(9)	21.4951(9)	15.9660(4)
b (Å)	13.9271(12)	10.1366(8)	11.8211(10)
c (Å)	15.0890(13)	15.8978(9)	7.2149(9)
α (°)	90	90	90
β (°)	116.827(5)	122.381(6)	100.175(4)
γ (°)	90	90	90
V (Å ³)	2875.4(4)	2925.3(3)	1340.3(2)
Z	6	4	4
μ (mm ^{−1})	1.203	0.839	1.642
F(000)	1482	1628	676
T _{min} ; T _{max}	0.752; 0.835	0.874; 0.960	0.741; 0.892
h; k; l min, max	−19, 18; −18, 16; −19, 19	−26, 25; −12, 12; −19, 19	−20, 20; −14, 15; −8, 9
θ _{min} ; max (°)	1.49; 27.50	2.40; 25.50	2.16; 27.49
Reflections number	20670	11932	10918
Total (R _{int}) ^a	6504 (0.0458)	2686 (0.0787)	3028 (0.0482)
gt [I > 2σ(I)]	3445	1828	1966
Number of Parameters	394	125	175
Max/min τ (e Å ^{−3})	0.683/−0.371	1.056/−0.596	0.723/−0.720
GOF ^b	1.073	1.074	1.070
R ^c /wR ^c	0.0596/0.1160	0.0972/0.2525	0.0505/0.1083

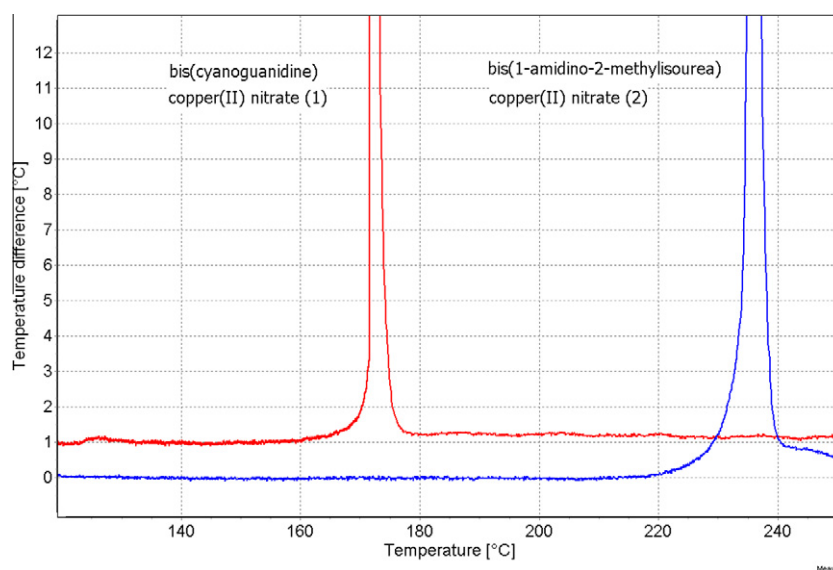
^a $R_{\text{int}} = \sum |F_o^2 - F_{o,\text{mean}}^2| / \sum F_o^2$.

^b $S = [\sum (w(F_o^2 - F_c^2)^2) / (N_{\text{diff}} - N_{\text{param}})]^{1/2}$.

^c Weighting scheme: $w = [\sigma^2(F_o^2) + (w_1P)^2 + w_2P]^{-1}$, where $P = [\max(F_o^2) + 2F_c^2]$, $R(F) = \sum ||F_o| - |F_c|| / \sum |F_o|$, $wR(F^2) = [\sum (w(F_o^2 - F_c^2)^2) / (\sum w(F_o^2)^2)]^{1/2}$.

Table 2Results of syntheses and DTA characteristics of complexes **1**–**17**.

Complex	Yield (%)	Procedure	Melting point ^a (°C)	Start of dec., DTA (°C)	Max. of dec., DTA (°C)
1	97	–	>360	159	172
2	95	A	>360	211	235
	99	B			
3	97	A	>360	211	250
	98	B			
4	99	B	>360	205	248
5	99	B	>360	208	236
6	83	A	184–186	169	180
7	91	B	>360	194	225
8	82	A	162–167	153	166
9	90	A	>360	238	264
	29	C ^b			
10	48	A	>360	227	260
	63	B			
11	51	B	>360	232	258
12	75	B	281–282	242	267
13	75	B	283–285	241	266
14	73	B	238–241	188	236
15	63	B	>360	242	263
16	73	B	>360	250	270
17	64	A	232–236	160	239

^a Kofler bench.^b The method C was used only for **9**, using the reaction of 1,1-dimethylbiguanide with copper nitrate trihydrate (for procedure, see Section 2.4.1).**Fig. 2.** DTA thermogram of compounds **1** and **2**.

reflect the π -electron conjugation through the system. These N–C atoms separations are close to the appropriate values found in the literature for highly delocalized systems [45]. In **4**, two molecules are present, one with C_i symmetry. In the crystal, one dimensional chains along [010], and two-dimension networks in plane (10–4) are formed via N–H...O hydrogen bonds. There are also π ... π stacking interactions with a centroid-to-centroid distance of 3.841(2) Å. On the other hand, there is only one molecule of **13** present having C_i symmetry. In the crystal of **13**, a three-dimensional network is formed via N–H...O hydrogen bonds. There are also C–H... π interactions present. The channels are occupied by the disordered solvent molecules of crystallization. Two molecules of **19** are present and both have C_i symmetry. In the crystal, a three-dimensional network is formed via N–H...O, O–H...N and N–H...N hydrogen bonds. There are also C–H... π interactions present. Here the channels are occupied by the methanol solvent molecules of crystallization.

The complexes **4** and **13** are formed by ion pairs of doubly chelated copper metal center by two neutral ligands and two nitrate

anions out of the primary coordination sphere of the metal atom (Figs. 5 and 6).

The complex **19** (Fig. 7) is formed by two monoanionic ligands bonded to the copper atoms and the ligand is deprotonated at N3 atom. This is also seen in the supramolecular arrangement of the complexes mentioned, 3D structures are formed in the cases of **13** (Fig. 8) and **19** (Fig. 9), where the planar L_2Cu moieties are joined by and nitrate anions in complex **13** and methanol molecules solvating the complex **19**. 2D structure is found for the complex **4** (Fig. 10). There are few differences in bond distances and interatomic angles found for complex **19** and the rest of ionic complexes on the other hand. The major difference is found in the Cu–N distances, where a bit shorter ones (~ 0.04 Å) were observed in the case of **19**. The same trend is also found for C1–N3 and N3–C2 distances in **19** and related distances in the rest of the complexes, on the other hand the longer distances C1–N1 and C2–N2 for imino bonds are longer by ca. 0.03 Å in **19**. The N–Cu–N angles are very close in all complexes, but the C1–N3–C2 angles

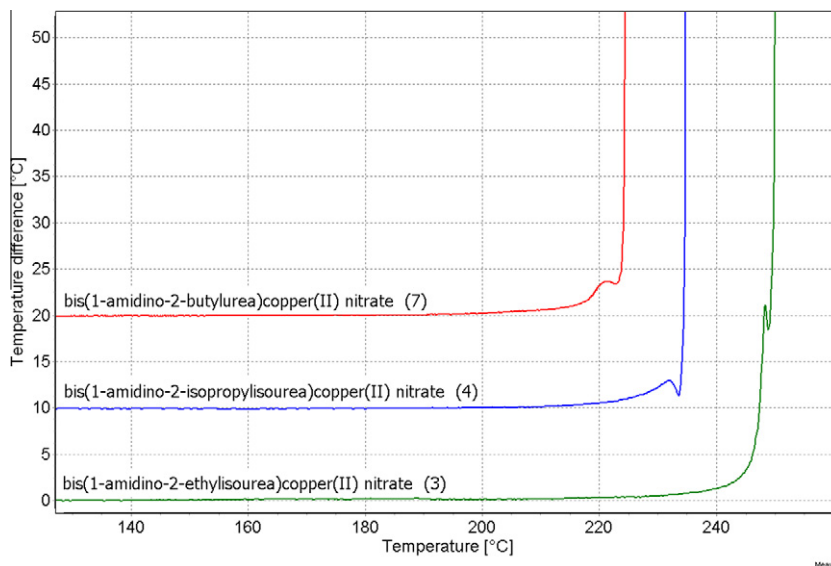


Fig. 3. DTA thermogram of 3, 4 and 7.

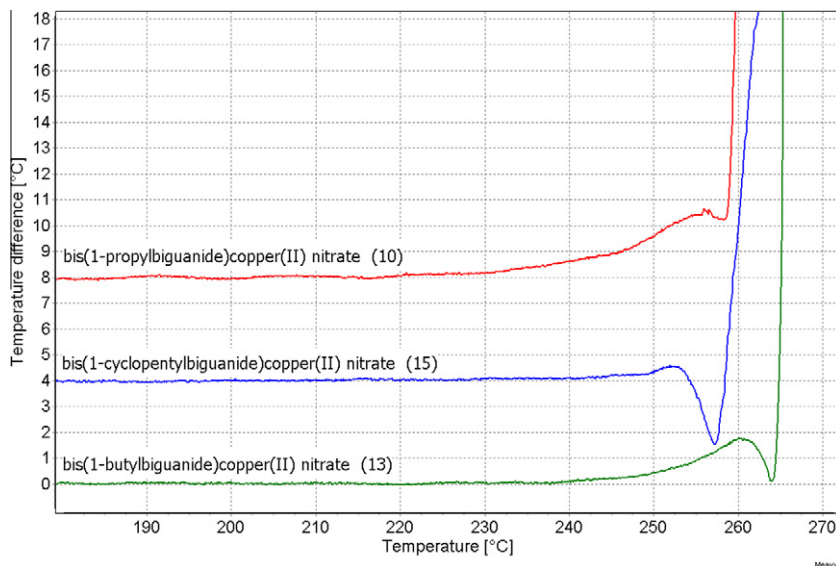


Fig. 4. DTA thermogram of 10, 13 and 15.

Table 3

Heats of combustion and enthalpies of formation of the complexes 1–17.

Complex Y=	Heat of combustion (kJ mol ⁻¹)	Heat of formation (kJ mol ⁻¹)	Heat of formation (kJ kg ⁻¹)
1	–2380	–500	–1410
2	–3840	–960	–2300
3	–4770	–1390	–3110
4	–6190	–1330	–2800
5	–6240	–1280	–2680
6	–6030	–960	–1960
7	–7540	–1340	–2660
8	–9540	–1130	–1980
9	–5750	–690	–1560
10	–7040	–770	–1630
11	–6740	–500	–1060
12	–8320	–850	–1700
13	–8300	–880	–1740
14	–8250	–920	–1830
15	–9300	–670	–1280
16	–10500	–810	–1460
17	–10970	–910	–1640

seem to be wider in ionic complexes by ca. 7°. There is an extensive H-bonding (Table 4) in all structures producing appropriate supra-molecular arrangements.

The *n*-butyl group in **13** is disordered and two carbon atoms are split into two positions and treated isotropically. There is disordered solvent (methanol) in the structure of **13**. Attempts were made to model this disorder or split it into two positions, but were unsuccessful. PLATON/SQUEZZE [46] was used to correct the data for the presence of disordered solvent. A potential solvent volume of 736 Å³ was found. One hundred and fifty-two electrons per unit cell worth of scattering were located in the void. The calculated stoichiometry of solvent was calculated to be eight molecules of methanol per unit cell which results in 144 electrons per unit cell.

3.3. Mass spectra

Molecular weights of studied compounds are confirmed based on the presence of deprotonated molecules [M–H][–] and adducts

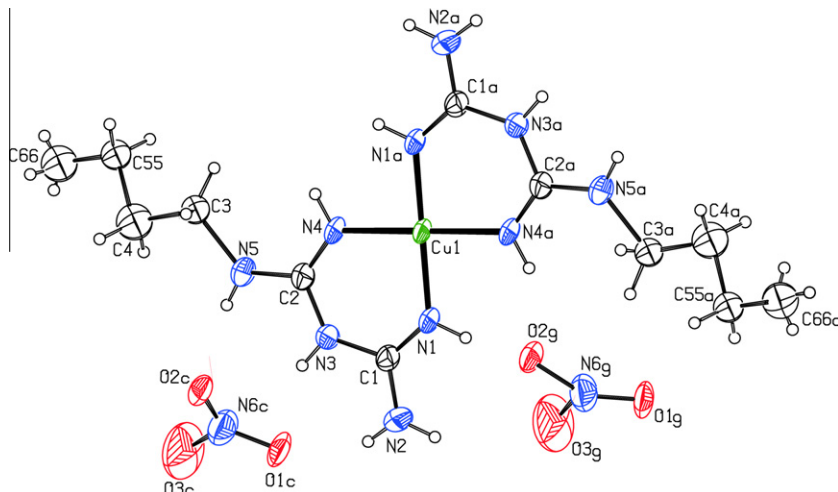


Fig. 5. The molecular structure of **13**, ORTEP view, 30% probability level. Positional disorders of *n*-Bu chains are omitted for clarity. Selected interatomic distances (Å) and angles (°): Cu1 N1 1.926(5), N1 C1 1.293(8), C1 N3 1.361(7), N3 C2 1.359(8), C2 N4 1.295(9), Cu1 N4 1.954(5), C1 N2 1.331(8), C2 N5 1.352(8); N4 Cu1 N1 89.3(2), Cu1 N1 C1 130.1(4), N1 C1 N3 120.9(6), C1 N3 C2 129.5(6), N3 C2 N4 121.2(5), C2 N4 Cu1 128.9(4).

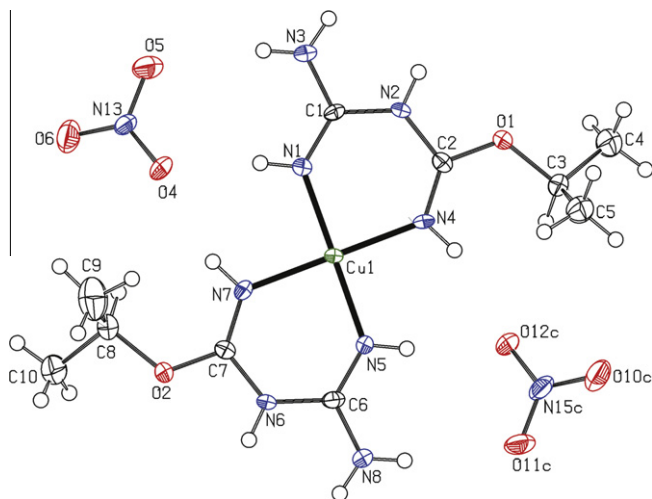


Fig. 6. The molecular structure of **4**, ORTEP view, 50% probability level. The second independent molecule is omitted for clarity. Selected interatomic distances (Å) and angles (°): Cu1 N1 1.931(3) (1.942(3)), N1 C1 1.300(5) (1.292(5)), C1 N2 1.361(5) (1.374(6)), N2 C2 1.369(5) (1.368(5)), C2 N4 1.270(5) (1.281(6)), N4 Cu1 1.973(4) (1.957(4)), Cu1 N5 1.929(3), N5 C6 1.298(5), C6 N6 1.372(6), N6 C7 1.365(5), C7 N7 1.283(5), N7 Cu1 1.975(4), C1 N3 1.347(5) (1.348(5)), C2 O1 1.325(5) (1.323(5)), C6 N8 1.340(5), C7 O2 1.334(5); N4 Cu1 N1 88.71(15) (88.87(15)), Cu1 N1 C1 129.9(3) (130.0(3)), N1 C1 N2 122.4(4) (122.1(4)); C1 N2 C2 126.5(4) (126.1(4)), N2 C2 N4 124.1(4) (124.3(4)), C2 N4 Cu1 128.3(3) (128.2(3)), N5 Cu1 N7 88.37(15), Cu1 N5 C6 131.2(3), N5 C6 N6 121.5(4), C6 N6 C7 126.4(4), N6 C7 N7 124.4(4), C7 N7 Cu1 127.9(3).

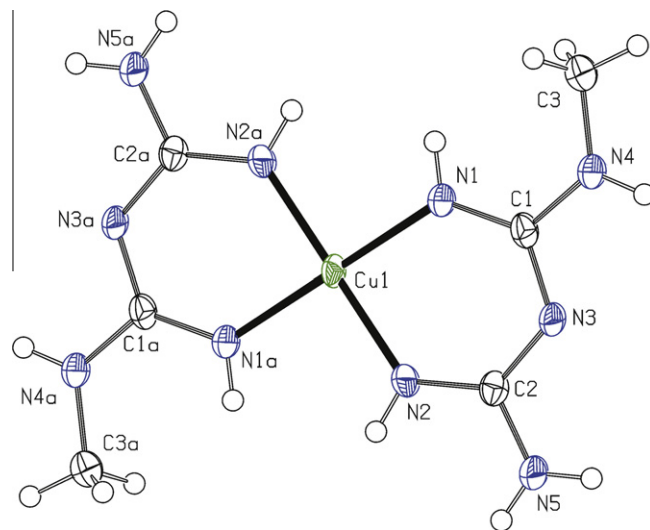


Fig. 7. The molecular structure of **19**, ORTEP view, 50% probability level. The second independent molecule and solvent (methanol) are omitted for clarity. Selected interatomic distances (Å) and angles (°): Cu1 N1 1.937(3) (1.931(3)), N1 C1 1.323(5) (1.320(5)), C1 N3 1.353(6) (1.368(6)), N3 C2 1.350(5) (1.335(6)), C2 N2 1.317(5) (1.321(5)), N2 Cu1 1.923(4) (1.932(4)), C1 N4 1.358(5) (1.348(5)), C2 N5 1.360(6) (1.373(6)); N2 Cu1 N1 88.23(15) (87.83(16)), Cu1 N1 C1 128.5(3) (128.8(3)), N1 C1 N3 126.0(4) (125.8(4)), C1 N3 C2 121.6(3) (121.7(4)), N3 C2 N2 126.4(4) (126.0(4)), C2 N2 Cu1 128.8(3) (128.9(3)).

with a nitrate group $[M+NO_3]^-$ in the negative-ion full scan mass spectra. On the other hand, the positive-ion full scan mass spectra provide information only about the cationic part of molecules formed after the loss of the nitrate group $[M-HNO_3-NO_3]^+$ or $[M-2NO_3]^{2+}$ as illustrated in Fig. 11. The structure of Y substituents (side chains) is determined by the specific neutral losses observed in the full scan and tandem mass spectra (see Section 2). Considering the differences between ion series of individual compounds, the origin of neutral losses can be assigned to the basic skeleton of ligands or the Y side substituent by the comparison of similar types of fragment ions (e.g. differences between MWs of compounds **10** and **11** is four mass units, such that the neutral loss containing one side chain will result in a pair of fragment ions

differing by two mass units, i.e. m/z 262 $[M-HNO_3-NO_3-CH_2N_2-C_3H_4]^+$ for **11** and m/z 264 $[M-HNO_3-NO_3-CH_2N_2-C_3H_6]^+$ for **10**, etc.). The presence of polyisotopic copper in particular ions can be further verified by the comparison of experimental isotopic distributions with the theoretical ones. Detailed interpretation of tandem mass spectra can be also used to distinguish compounds with the identical elemental composition as shown in MS³ spectra of ions at m/z 334 for compounds **12**, **13** and **14**. Ions at m/z 305, m/z 278 and m/z 262 show the main difference among the spectra of these three compounds. The ion at m/z 305 formed by the neutral loss of ethyl is not observed for compound **12** with respect to the structure of isobutyl substituent, while the loss of butane (m/z 278) cannot be present in the spectra of compound **14**, for which the loss of $N(CH_2CH_3)$ radical is more probable (see Fig. 12).

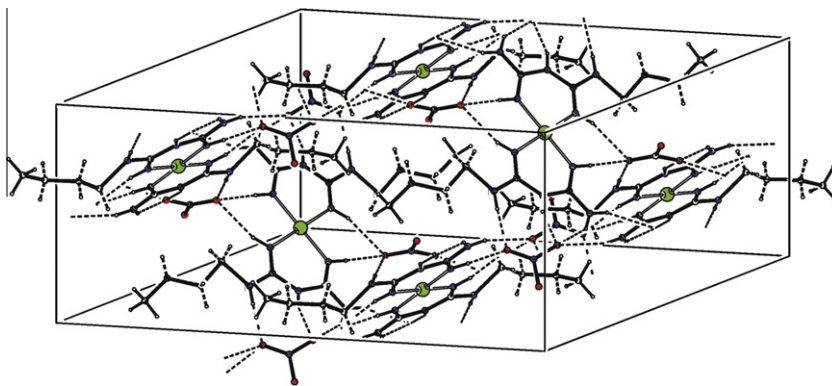


Fig. 8. H-bonding interactions found in the solid state structure for **13**. The *c* face view.

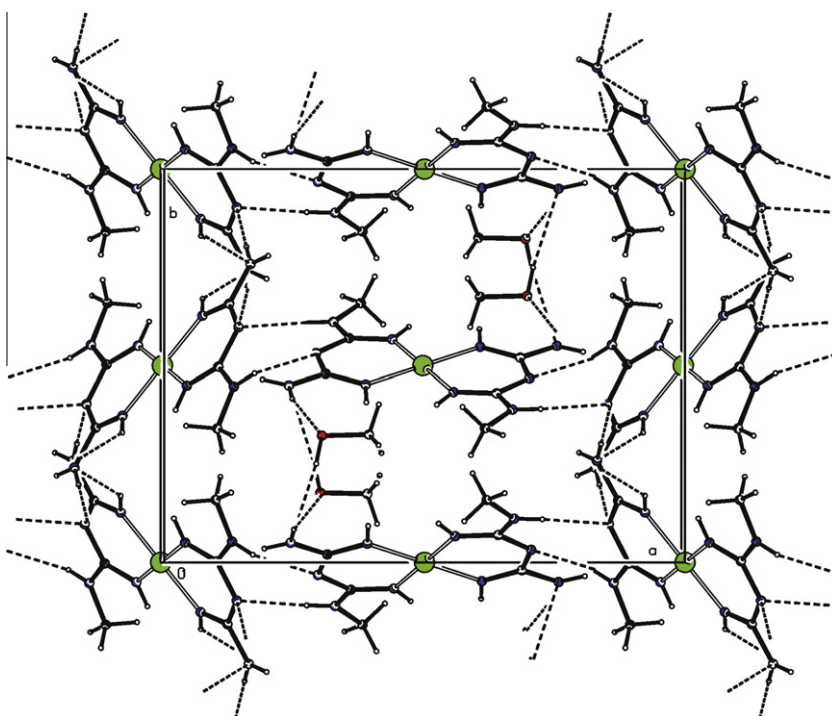


Fig. 9. H-bonding interactions found in the solid state structure for **19**. View along the *z* axis.

3.4. Infrared spectroscopy

The aim of the analysis is to identify which of the vibrational modes in the molecule give rise to the observed absorption bands in the FTIR spectra of the derivatives of copper biguanide complexes. The observed absorption bands for amidinoisourea and biguanide complexes are summarized in Tables 5 and 6, respectively. The assignments of absorption bands have been made after comparing with structurally similar compounds and by the change occurring due to substitution of some functional groups in the ligands [47,48].

A number of peaks appearing in the spectral region 3500–3100 cm^{-1} are presented due to the stretching vibrations of the NH and NH_2 bonds [49]. These bands are also observed in the substituent groups $\text{Y}=\text{O}-\text{R}$ and $\text{Y}=\text{N}-\text{R}$. The positions of the peaks shift according to the different substituents (see Tables 5 and 6). A larger shift is observed in the case of functional group NH than for the NH_2 group. Absorption bands due to the stretching vibrations of C–H on the C=C double bond are localized in the spectral

range 3000–3100 cm^{-1} : for the allyl group of **6** in the peak position 3083 cm^{-1} and for the allyl group of **11** in the peak position 3053 cm^{-1} . A similar peak is found for the CH stretching vibration in the aromatic ring of **8** – 3035 cm^{-1} . In the region 1700–1430 cm^{-1} three bands are observed [49,50], near 1660, 1550 and 1480 cm^{-1} . These are probably due to the stretching vibration of the bond N–C–N, C=NH and the deformation vibration of NH. In these positions, peaks are presented in the case of a complex bond with copper. The shift position of these peaks (due to different substituent) is low. If the peak is at a higher wave number (e.g. near 1690 cm^{-1}) the free ligand is presented as an impurity. During the formation of a chelate ring with copper, two peaks appear around 1330 and 1290 cm^{-1} . A number of peaks in the spectral ranges 1200–1030 cm^{-1} $\nu(\text{C}-\text{N})$ and 940–740 cm^{-1} (wagging vibration N–H) are only identifiable with difficulty. Stretching vibration of C–O–R produces a peak around 1200 cm^{-1} . Presence of a nitrate anion forms a peak near 1380 cm^{-1} . The comparison of IR spectra of **5** and **10** is illustrated in Fig. 13.

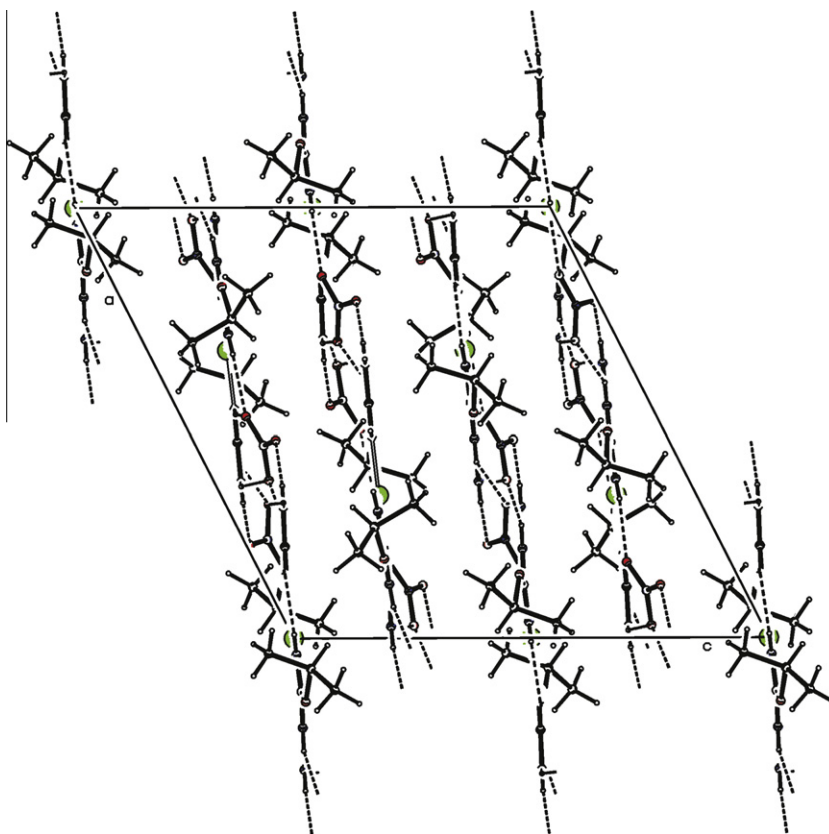


Fig. 10. H-bonding interactions found in the solid state structure for **4**. View along the y axis.

Table 4
Hydrogen bonds for **4**, **13** and **19** (Å, °).

	D–H...A	<i>d</i> (H...A)	<i>d</i> (D...A)	∠(DAH)	Symm. transformation
4	N(4)–H(4)...O(12)	2.21	3.038(5)	162.3	$x, y - 1, z$
	N(8)–H(8A)...O(11)	2.47	3.280(6)	157.7	$x, y - 1, z$
	N(5)–H(5)...O(12)	2.06	2.918(5)	172.1	$x, y - 1, z$
	N(6)–H(6)...O(11)	2.11	2.942(5)	163.4	$-x, y - 1/2, -z + 1/2$
	N(8)–H(8B)...O(10)	2.07	2.919(5)	170.6	$-x, y - 1/2, -z + 1/2$
	N(2)–H(2)...O(8)	2.19	2.986(5)	153.3	$-x + 1, y - 1/2, -z + 1/2$
	N(2)–H(2)...O(9)	2.64	3.385(5)	145.7	$-x + 1, y - 1/2, -z + 1/2$
	N(3)–H(3B)...O(9)	2.07	2.918(5)	170.3	$-x + 1, y - 1/2, -z + 1/2$
	N(9)–H(9)...O(7)	2.03	2.886(5)	171.7	$x, y + 1, z$
	N(12)–H(12A)...O(8)	2.40	3.238(6)	164.9	$x, y + 1, z$
	N(10)–H(10)...O(5)	2.13	2.961(5)	161.1	$-x + 1, y + 1/2, -z + 1/2$
	N(12)–H(12B)...O(6)	2.10	2.949(5)	171.8	$-x + 1, y + 1/2, -z + 1/2$
	N(11)–H(11)...O(7)	2.27	3.093(5)	161.6	$-x, -y + 1, -z$
	N(1)–H(1)...O(4)	2.05	2.896(5)	168.7	–
	N(7)–H(7)...O(4)	2.20	3.025(5)	162.0	–
	N(3)–H(3A)...O(5)	2.52	3.326(6)	155.8	–
13	N(1)–H(1)...O(2)	2.06	2.918(6)	174.3	$x, -y + 1, z - 1/2$
	N(4)–H(4)...O(2)	2.28	3.116(7)	163.4	$-x + 1/2, y - 1/2, -z + 3/2$
	N(3)–H(3)...O(1)	1.96	2.788(7)	160.7	$x, y - 1, z$
	N(3)–H(3)...N(6)	2.61	3.463(9)	171.7	$x, y - 1, z$
	N(3)–H(3)...O(2)	2.66	3.401(7)	144.7	$x, y - 1, z$
	N(2)–H(2B)...O(1)	2.22	2.964(8)	145.4	$x, y - 1, z$
	N(5)–H(5)...O(2)	1.99	2.849(9)	176.2	$x, y - 1, z$
	N(2)–H(2A)...O(1)	2.29	2.907(7)	129.1	$-x + 1, y - 1, -z + 3/2$
19	N(2)–H(2)...N(5)	2.59	3.337(5)	145.8	$x, -y + 3/2, z - 1/2$
	N(4)–H(4)...N(8)	2.20	3.031(5)	163.6	$x, y, z + 1$
	N(5)–H(5A)...N(3)	2.12	2.982(5)	176.9	$x, -y + 3/2, z - 1/2$
	N(9)–H(9)...N(3)	2.17	3.026(5)	175.0	$x, y, z - 1$
	N(10)–H(10B)...O(1A)	2.38	3.219(9)	164.7	$x, -y + 1/2, z + 1/2$
	O(1A)–H(1A)...N(10)	2.55	3.489(9)	165.0	–

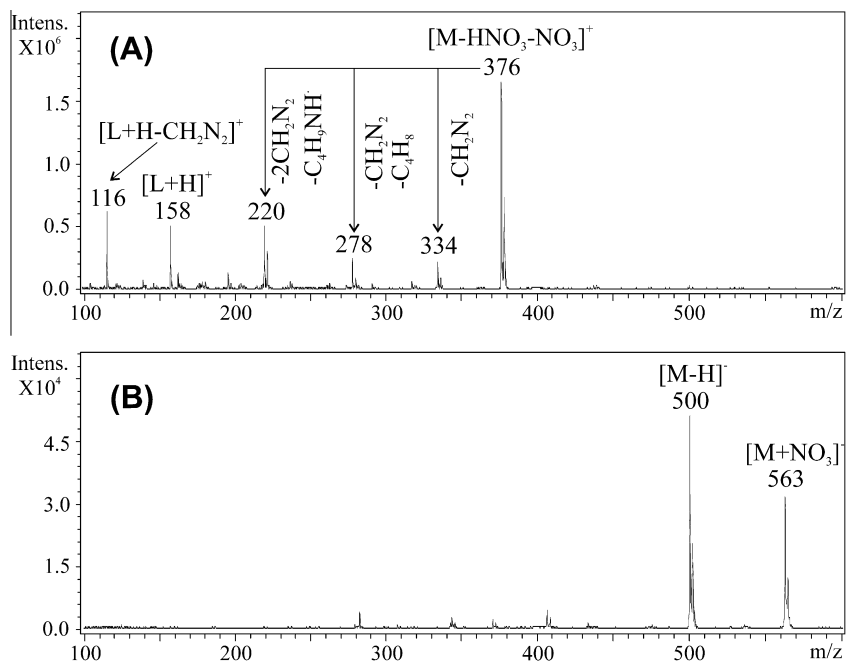


Fig. 11. Electrospray positive-ion (A) and negative-ion (B) full scan mass spectra of compound 12.

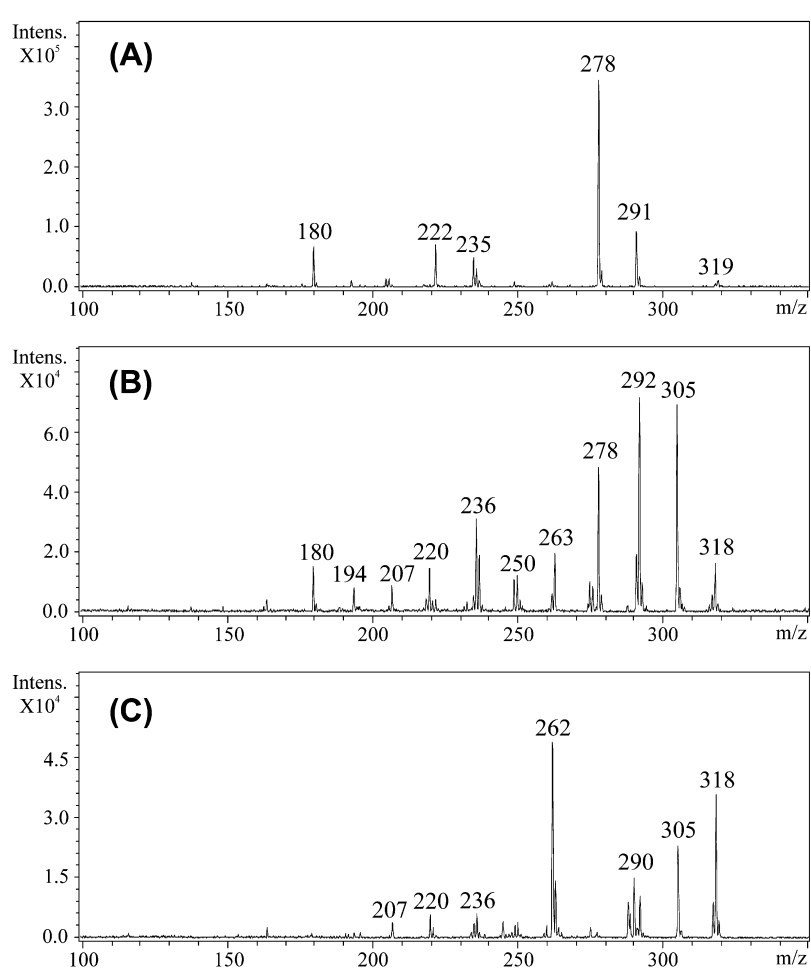


Fig. 12. MS^3 spectra of fragmentation path m/z 376–334 for compounds 12 (A), 13 (B) and 14 (C).

Table 5Characteristic IR absorption bands (cm^{-1}) for biguanide Cu complexes of O–R substituents.

Compound/band assignment	2	3	4	5	6	7	8	9
$\nu(\text{NH})$		3398w	3401w	3461w	3388w	3385w	3439m	3419m
$\nu_{\text{as}}(\text{NH}_2)$	3352s	3338m	3341m	3308m	3333m	3343m	3343m	3358m
$\nu(\text{NH})$	3255m	3243m	3247m	3271m	3268w	3272m	3288m	3269m
$\nu_{\text{s}}(\text{NH}_2)$	3180s	3203m	3208m	3190m	3177m	3177m	3157m	3219m
$\nu(\text{CH}=\text{CH})$					3084w			3035w
$\nu_{\text{as}}(\text{CH}_3)$	3011m	2998m	2993m	2973w		2964w		
$\nu_{\text{as}}(\text{CH}_2)$		2950w		2950vw		2938w	2940m	2941w
$\nu_{\text{s}}(\text{CH}_3)$		2872w		2880w		2873w		
$\nu_{\text{s}}(\text{CH}_2)$							2859m	
$\nu(\text{C}=\text{N})$	1691s						1676s	
	1664vs	1665vs	1669vs	1669vs	1678vs	1671vs	1638vs	1670vs
							1595m-s	
	1556m	1558m	1554m	1558m	1560m	1547m	1550m	1555m
	1504m	1494m	1489m	1488m-w	1501m	1496m	1497m	1497m
Chelate ring	1340s	1327m-s	1337s	1332m-s	1354m-s	1337s	1331m	1352s
	1293m	1284m	1283m	1280m	1290m	1287m	1303m	1286m
$\nu_{\text{s}} \text{ C}-\text{O}-\text{R}$	1209s	1217s	1213s	1224s-m	1217m-s	1212s	1208s	1205s
$\nu(\text{CN})$	1125m	1130w	1127w	1128w	1129w	1120m	1129w	1117m
	1053w	1052w	1051w					
CH on $\text{C}=\text{C}$, out of plane					988w			
N–H wagging	817m	832m	831m	822m	823w	825m	824m	823m
$\text{C}=\text{C}$ arom. ring out of plane								694m
$\delta \text{ C}-\text{N}-\text{C}$	518m	520m	531w	534w	520m	522m	519m	506m
$\nu(\text{NO}_3^-)$	1396s	1379m-s	1386m	1398m	1382m-s	1395m-s	1394s	1378sh.

ν_{as} , stretching vibration asymmetric; ν_{s} , stretching vibration symmetric; δ , deformation vibration intensity of band; vs, very strong; s, strong; m, medium; w, weak; vw, very weak; sh, shoulder.

Table 6Characteristic IR absorption bands (cm^{-1}) for biguanide Cu complexes of N–R substituents.

Compound/band assignment	9	10	11	12	13	14	15	16	17
$\nu_{\text{as}}(\text{NH})$		3461w	3472m	3407m	3413vw		3461m		
$\nu_{\text{as}}(\text{NH}_2)$	3384s	3355m	3369m	3364m	3363m	3375m	3369m	3366m	3369m
$\nu(\text{NH})$	3192s	3226w		3223m-s	3225m	3202m	3223w	3228m	3189m
		3120w	3120m	3114m			3110m	3119w	
$\nu_{\text{s}}(\text{NH}_2)$	3268vs	3271m	3281s	3277m-s	3281m	3273m	3267m-s	3285m	3271s
$\nu(\text{CH}=\text{CH})$			3053w						
$\nu_{\text{as}}(\text{CH}_3)$	2972w	2967w		2960m	2960w	2980w			2963m
$\nu_{\text{as}}(\text{CH}_2)$		2940w			2935w	2938w	2947m	2932m	2933m
$\nu_{\text{s}}(\text{CH}_3)$		2882vw		2874m	2874w				
$\nu_{\text{s}}(\text{CH}_2)$					2860vw		2879w	2857m-w	2874m
$\nu(\text{C}=\text{N})$	1687s		1694s		1687m	1684s	1695m	1684m	
	1639s	1670vs	1665vs	1662vs	1660vs	1654m	1664s	1665vs	1673s
						1624s	1576m-s		1618vs
	1544m	1577m	1576s	1565m-s	1566m-s	1527m	1543m-s	1567s-m	1538m-w
	1517s	1481w	1474w	1471m	1472w	1504s	1475w	1480w	1508m
Chelate ring	1484m	1336m	1342vs	1327s	1330m	1334vs	1332m-s	1328m	1332s
	1347vs						1321m-s		
			1282m	1276m-s	1283m	1272m	1276m-s	1280m-w	1270m
	1277m	1250m-s	1252m-s	1240s	1243m	1247m	1251s	1242m	1229m
$\nu(\text{CN})$	1200m	1149w	1140w	1174m-w	1149w	1176m	1154w	1150w	1173m
		1054w	1051w	1052w	1053w	1084m	1085w	1065w	1097m
	1075m	1020w		1040w	1036w		1050m	1052w	
CH on $\text{C}=\text{C}$ out of plane	1049w		994w						
N–H wagging		981w	984w		972w	967m		967w	973w
	970w	819m	818m	823m	824m	823m	822m	832m	831m-w
	821w	796m-w	799m	808m	803m	796m	813m	805m	
$\delta \text{ C}-\text{N}-\text{C}$	804m	567w	580w			593m		590w	
		533w	516w	541m	523m	536m		520m	542m
$\nu(\text{NO}_3^-)$	515w	1392s	1382vs	1377s	1372m	1381s	1383s	1380s	1382m
	1380sh					1362m			

ν_{as} , stretching vibration asymmetric; ν_{s} , stretching vibration symmetric; δ , deformation vibration intensity of band; vs, very strong; s, strong; m, medium; w, weak; vw, very weak.

All the bands mentioned confirm the formation of a complex bond between copper and two biguanide ligands with the nitrogen in the groups $-\text{C}=\text{NH}$ notwithstanding substitution of the ligand.

4. Conclusions

Copper(II) complexes of amidinoisourea and biguanidine $[\text{Cu}\{\text{NH}_2(\text{C}=\text{NH})\text{NH}(\text{C}=\text{NH})\text{Y}\}]_2 (\text{NO}_3)_2$, have been prepared and

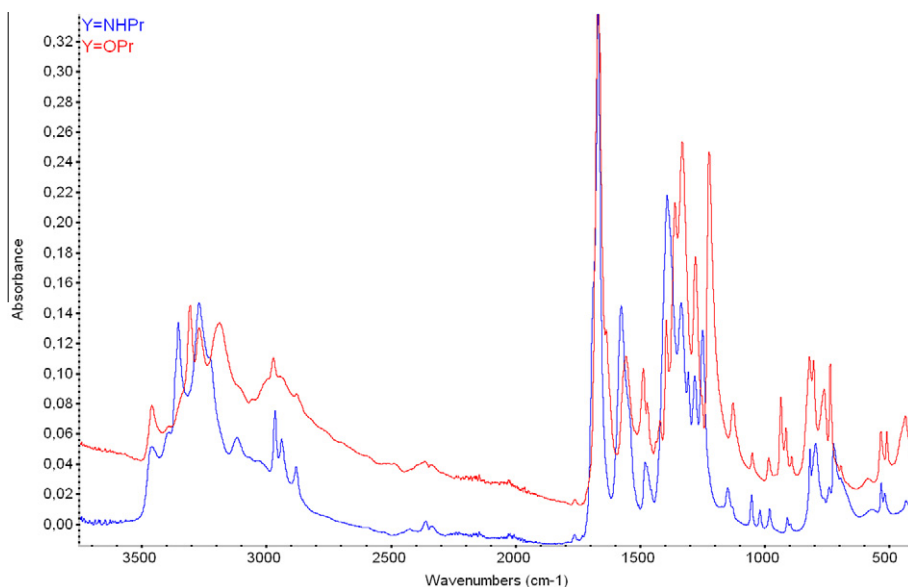


Fig. 13. Comparison of IR spectra of **5** (Y = OPr, blue) and **10** (Y = NHPr, red). (Color online.)

characterized by elemental analysis, X-ray crystallography, mass spectroscopy and FTIR.

Decomposition temperatures determined by DTA indicate/predict point to good thermal stability. Biguanide complexes have higher decomposition temperatures than amidinoisoureas. The choice of the substituent Y in the complexes (**2–17**) may influence the crucial properties for the purpose of inflating systems: carbon/hydrogen/nitrogen content and enthalpy of formation. The biguanide complexes and the complexes with substituents having double bonds or cycles generally have higher enthalpy of formation.

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Appendix A. Supplementary data

CCDC 871875, 871874 and 871873 contains the supplementary crystallographic data for **4**, **13** and **19**, respectively. 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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