

Synthesis, structure and spectroscopic properties of bis(triphenylphosphane)iminium (phenylacetylido)(cyanido)aurate(I) monoacetone monohydrate, (PPN)[Au(C≡N)(C≡C–C₆H₅)]·H₂O·(CH₃)₂CO and bis(triphenylphosphane)iminium (*t*-butylacetylido)(cyanido)aurate(I) monohydrate, (PPN)[Au(C≡N)(C≡C–C₄H₉)]·H₂O

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ABSTRACT

Two new compounds containing the (acetylido)(cyanido)aurate(I) anion are reported. Their solid-state structures with the monocation PPN, bis(triphenylphosphane)iminium, are reported as a product containing a water molecule and an acetone molecule for the phenylacetylido compound, and as a monohydrate in the case of the *t*-butylacetylido compound. The gold atom is linearly coordinated with normal Au–C bonds in both cases (1.97–1.99 Å). Hydrogen bond chains are found from N to water and from water to acetone, with H bond D···A contact distances of 2.92 Å (O···O) and 3.01 Å (O···N) for the phenylacetylido compound. The PPN cation has normal bond lengths in both compounds and no short contacts with other atoms in the lattice are observed.

The luminescence properties of both compounds have been measured as solid powders. The phenylacetylido compound shows medium strength emission with two peaks at 431 and 454 nm when excited at 310 nm. The excitation spectra monitored at 431 and 454 nm, respectively, show similar spectra with a broad band maximum at 310–317 nm. Surprisingly, the *t*-butylacetylido compound displays negligible luminescence.

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1. Introduction

Luminescent d¹⁰ coinage metal compounds have been actively investigated in recent years, with a focus on their emission properties in relation to the electronic structure of the compounds [1–6]. Especially Ag(I) and Au(I) complexes have been studied.

Cyanido gold compounds are known to have a linear coordination geometry and often also show interesting luminescent properties [7–10], even when other metals are present [3–5,11–14]. In previous studies from our laboratories, variations with mixed-metal compounds were reported in which some or all of the cyanide

ligands are acting as bridging ligands between two metal ions (including Cu and Ag) [15–17].

We now have extended this study by changing one of the cyanide ligands to an acetylido group, and both aromatic and an aliphatic substituents were chosen. To minimize the intermolecular interactions, the very large cation PPN (bis(triphenylphosphane)iminium), was selected as the counter cation. This paper reports the synthesis, structure and luminescence properties of two representative new Au compounds, having an acetylido co-ligand, i.e. one aromatic and one aliphatic.

2. Experimental part

Starting materials were used as purchased without further purification. The salt bis(triphenylphosphane)iminium chloride, PPNCl, was used as commercially available (Aldrich; Analar grade). Potassium cyanide was also used as commercially available (Koch-Light

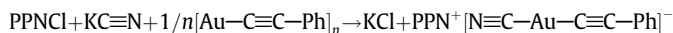
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Labs. Ltd. grade). Hexane, acetone and methanol were used as commercially available (BDH-Analar grade) and kept over molecular sieves. The compounds $[\text{Au}-\text{C}\equiv\text{C}-\text{Ph}]_n$ and $[\text{Au}-\text{C}\equiv\text{C}-\text{Bu}^t]_n$ were made as described by Coates and Parkin [18] and detailed below.

Syntheses of $[\text{Au}(\text{C}\equiv\text{C}-\text{Ph})]_n$ and $[\text{Au}(\text{C}\equiv\text{C}-\text{Bu}^t)]_n$. An aqueous solution of KBr (4.5 g, 3.78 mmol) was added to an aqueous-acetone solution (1:1 ratio) of HAuCl_4 (3.0 g of $\text{HAuCl}_4 \cdot x\text{H}_2\text{O}$, 51% Au, 7.77 mmol). A clear deep red solution was obtained. The mixture was cooled at 10 °C with water/ice and then the resulting solution was treated dropwise with a fresh aqueous solution of SO_2 until the color of the solution became light red, and was left stirring for 5 min without further addition. Next, an aqueous solution of SO_2 was added dropwise followed by a color change to pale-yellow. Subsequent addition of acetylene (7.77 mmol, $\text{HC}\equiv\text{C}-\text{Ph}$: 0.850 mL, $\text{HC}\equiv\text{C}-\text{Bu}^t$: 0.955 mL) and sodium acetate (6.37 g, 7.77 mmol) led to the formation of an off-white precipitate within 1 h. The precipitate was separated by filtration and washed several times with water, ethanol and cold acetone, yielding $[\text{Au}(\text{C}\equiv\text{C}-\text{Ph})]_n$ (2.20 g, 95%), m.p. 150 °C (decomp.), IR as KBr disc: $\nu(\text{C}\equiv\text{C})$ 1962 cm^{-1} , or $[\text{Au}(\text{C}\equiv\text{C}-\text{Bu}^t)]_n$ (2.00 g, 92%), m.p. 170 °C (decomp.), IR as KBr disc: $\nu(\text{C}\equiv\text{C})$ 1960 cm^{-1} .

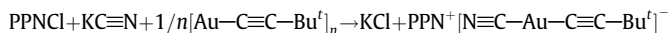
The new compound $\text{PPN}^+[\text{N}\equiv\text{C}-\text{Au}-\text{C}\equiv\text{C}-\text{Ph}]^-$ (compound 1) has been synthesized as follows: Gold(I) phenylacetylide, $[\text{Au}-\text{C}\equiv\text{C}-\text{Ph}]_n$ (0.298 g, 1 mmol) was added to a clear solution of bis(triphenylphosphane)iminium chloride, $[\text{N}(\text{PPh}_3)_2]^+\text{Cl}^-$ (0.574 g, 1 mmol) in methanol (30 mL). While stirring for 30 min a clear solution was formed, and subsequently potassium cyanide (0.065 g, 1 mmol) was added which dissolved within 10 min. After 20 min a yellow solid precipitated. The suspension was evaporated to dryness and the residue was extracted with acetone (20 mL). A grey precipitate was formed which was filtered off (KCl, 0.073 g, 97%). To the remaining clear solution hexane (35 mL) was added, and a crystalline material was collected in high yield (95%, 0.890 g). A single-crystal X-ray diffraction analysis revealed the composition $\{\text{PPN}^+[\text{N}\equiv\text{C}-\text{Au}-\text{C}\equiv\text{C}-\text{Ph}]^- \cdot \text{H}_2\text{O}(\text{acetone})\}$ ($\text{C}_{48}\text{H}_{43}\text{AuN}_2\text{O}_2\text{P}_2$), m.p. 120 °C. *Elemental analysis*: Calc. for $\text{C}_{48}\text{H}_{43}\text{AuN}_2\text{O}_2$: C, 61.41; H, 4.62; N, 2.98. Found: C, 63.15; H, 4.60; N, 3.15%. The found% C is 1.7% higher than calculated; this is not understood and is tentatively ascribed to an experimental aberration, as the crystal batch appears homogeneous, and the XRD analysis (vide infra), clearly shows one acetone in the lattice. Part of the recrystallized precipitate, when dried at 100 °C for 1 h, gave a white solid without solvent molecules in the crystal lattice analyzing for $[\text{N}\equiv\text{C}-\text{Au}-\text{C}\equiv\text{C}-\text{Ph}]^- \text{PPN}^+$ ($\text{C}_{45}\text{H}_{35}\text{AuN}_2\text{P}_2$), m.p. 132 °C, Found (Calc.): C, 62.31 (62.65); H, 4.18 (4.06); N, 3.00(2.25)%. FTIR: $\nu(\text{max})$ cm^{-1} (as KBr disk) 1282, 1262 (s, $\text{P}_2=\text{N}$), 1114 (s, $\text{P}-\text{C}$), 2139 (m, $\text{C}\equiv\text{N}$), 2113 (w, $\text{C}\equiv\text{C}$) cm^{-1} . The schematic equation of formation reads:



The new compound $\text{PPN}^+[\text{N}\equiv\text{C}-\text{Au}-\text{C}\equiv\text{C}-\text{Bu}^t]^-$ (compound 2) has been synthesized as follows: Gold *t*-butylacetylide (3,3-dimethylbutynyl)gold) $[\text{Au}-\text{C}\equiv\text{C}-\text{Bu}^t]_n$ (0.278 g, 1 mmol) was added to a clear solution of bis(triphenylphosphane)iminium chloride, $[\text{N}(\text{PPh}_3)_2]^+\text{Cl}^-$ (0.574 g, 1 mmol) in methanol (30 mL). While stirring for 30 min a clear solution was formed, and subsequently potassium cyanide (0.065 g, 1 mmol) was added which dissolved within 10 min. After 20 min a white solid precipitated. The suspension was evaporated to dryness and the residue was extracted with acetone (25 mL). A grey precipitate was formed which was filtered off (KCl, 0.070 g, 93%). To the remaining clear solution *n*-hexane (40 mL) was added, and a crystalline material was collected in high yield (90%, 0.774 g). A single-crystal X-ray diffraction analysis

revealed the composition $\{\text{PPN}^+[\text{N}\equiv\text{C}-\text{Au}-\text{C}\equiv\text{C}-\text{Bu}^t]^- \cdot \text{H}_2\text{O}\}$ ($\text{C}_{43}\text{H}_{41}\text{AuN}_2\text{OP}_2$), m.p. 135 °C. Compound 2 is isolated containing one molecule of water per formula unit. *Elemental analysis*: Found (calc.): %C: 59.84 (60.00), %H: 4.58 (4.76), %N: 3.26 (3.26), FTIR: $\nu(\text{max})$ cm^{-1} (KBr disk) 1283, 1261 (s, $\text{P}_2=\text{N}$), 1114 (s, $\text{P}-\text{C}$), 2137 (m, $\text{C}\equiv\text{N}$), 1983 (vw, $\text{C}\equiv\text{C}$) cm^{-1} .

The overall equation of formation for compound 2 is as follows:



The elemental analyses were performed by using a Perkin Elmer Series II-2400 analyzer and the FT-IR spectrum was recorded on a Thermo Scientific Nicolet iS10.

The excitation and emission spectra were recorded at room temperature using a Shimadzu RF-5301PC spectrofluorophotometer equipped with a solid-state sample holder. The excitation spectrum was recorded by constantly monitoring the emission spectrum at the wavelength of most intense luminescence while scanning the excitation wavelength from 220 to 400 nm. The excitation spectrum has been corrected for the response of the detector and light source.

Single crystals of $\text{C}_{48}\text{H}_{43}\text{AuN}_2\text{O}_2\text{P}_2$ (compound 1) and $\text{C}_{43}\text{H}_{41}\text{AuN}_2\text{OP}_2$ (compound 2) were collected from the synthetic batches. A suitable crystal was selected and measured on a Bruker APEX-II CCD diffractometer. Each crystal was kept at 153.2 K during data collection. Using Olex2 [19] the structures were solved with the Superflip [20–22] structure solution program by Charge Flipping and refined with the SHELXL [23] refinement package, using Least Squares minimization (see Tables 1 and 2).

3. Results and discussion

3.1. Synthesis and characterization

The two new compounds appeared to crystallize with lattice solvents, i.e. water and acetone for compound 1, and only water

Table 1
Crystal data and structure refinement for compound 1.

CCDC number	1030371
Empirical formula	$\text{C}_{48}\text{H}_{43}\text{AuN}_2\text{O}_2\text{P}_2$
Formula weight	938.75
Temperature (K)	153(1)
Crystal system	monoclinic
Space group	$P2_1/c$
<i>a</i> (Å)	9.8763(3)
<i>b</i> (Å)	18.6454(6)
<i>c</i> (Å)	22.8316(7)
α (°)	90
β (°)	97.3149(17)
γ (°)	90
Volume (Å ³)	4170.2(2)
<i>Z</i>	4
Calculated density (mg mm^{-3})	1.495
Absorption coefficient (mm^{-1})	3.645
<i>F</i> (000)	1880.0
Crystal size (mm^3)	$0.411 \times 0.243 \times 0.01$
Radiation	$\text{Mo K}\alpha$ ($\lambda = 0.71073$)
2θ range for data collection (°)	4.698–52.77
Index ranges	$-11 \leq h \leq 12$, $-23 \leq k \leq 23$, $-24 \leq l \leq 28$
Reflections collected	30964
Independent reflections	8499 [$R_{\text{int}} = 0.0382$, $R_{\text{sigma}} = 0.0393$]
Data/restraints/parameters	8499/0/501
Goodness-of-fit on F^2	1.161
Final <i>R</i> indexes [$I \geq 2\sigma(I)$]	$R_1 = 0.0420$, $wR_2 = 0.0818$
Final <i>R</i> indexes (all data)	$R_1 = 0.0531$, $wR_2 = 0.0850$
Largest difference in peak/hole (e Å^{-3})	1.43/−1.51

Table 2
Crystal data and structure refinement for compound **2**.

CDCC number	1030372
Empirical formula	C ₄₃ H ₄₁ AuN ₂ OP ₂
Formula weight	860.68
Temperature [K]	153(1)
Crystal system	triclinic
Space group	P $\bar{1}$
<i>a</i> (Å)	9.7089(5)
<i>b</i> (Å)	10.7157(6)
<i>c</i> (Å)	19.8687(10)
α (°)	85.235(2)
β (°)	81.067(2)
γ (°)	75.898(3)
Volume (Å ³)	1978.27(18)
<i>Z</i>	2
Calculated density (mg mm ^{−3})	1.445
Absorption coefficient (mm ^{−1})	3.833
<i>F</i> (000)	860.0
Crystal size (mm ³)	0.633 × 0.129 × 0.088
Radiation	Mo K α (λ = 0.71073)
2 θ range for data collection (°)	5.594–56.55°
Index ranges	−12 ≤ <i>h</i> ≤ 12, −11 ≤ <i>k</i> ≤ 14, −26 ≤ <i>l</i> ≤ 25
Reflections collected	18393
Independent reflections	9716 [<i>R</i> _{int} = 0.0438, <i>R</i> _{sigma} = 0.0525]
Data/restraints/parameters	9716/85/519
Goodness-of-fit on <i>F</i> ²	1.072
Final <i>R</i> indexes [<i>I</i> ≥ 2 σ (<i>I</i>)]	<i>R</i> ₁ = 0.0356, <i>wR</i> ₂ = 0.0919
Final <i>R</i> indexes (all data)	<i>R</i> ₁ = 0.0406, <i>wR</i> ₂ = 0.0947
Largest difference in peak/hole (e Å ^{−3})	1.81/−1.14

for compound **2**. In addition to elemental analyses, see exp. part, the compounds were also investigated by IR spectroscopy. All expected ligand and PPN bands were visible, and in particular the C≡N and C≡C triple bonds, near 2100 cm^{−1}, were easily detected. In the case of the phenylacetylide two bands were observed, namely at 2133 and 2113 cm^{−1}, whereas the *t*-butylacetylide showed a single band at 2137 cm^{−1}, suggesting the coordinated C≡N stretch to be at about 2135 cm^{−1}.

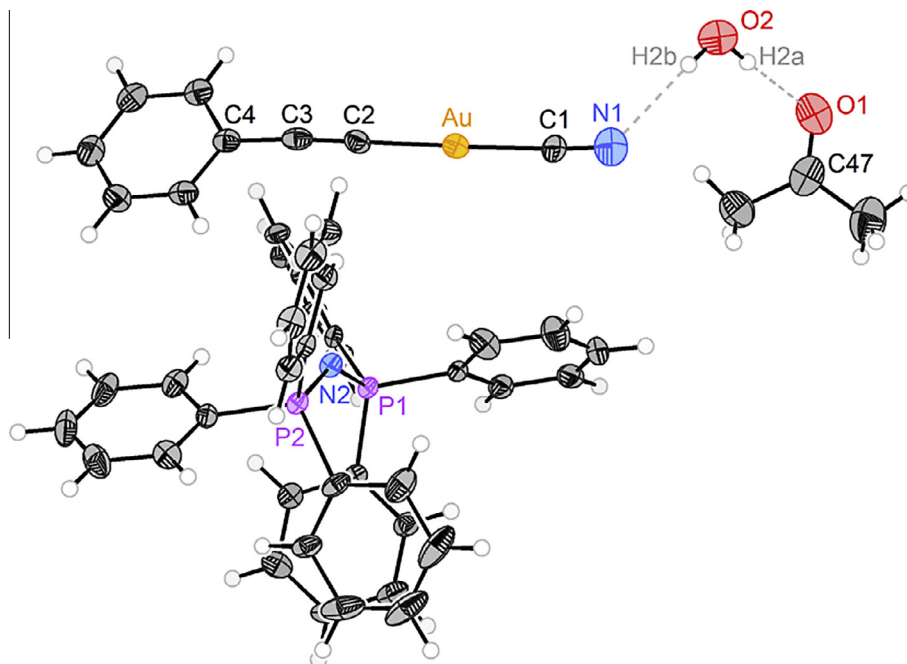


Fig. 1. Projection of cation, anion and lattice solvent molecules in compound **1** with thermal ellipsoid plot at the 50% levels of probability. Selected bond lengths [Å] and angles [°] are: Au–C1 1.971(6), Au–C2 1.990(5), C1–N1 1.158(8), C2–C3 1.204(7), C3–C4 1.429(7), N1...O2 3.009(8), O1...O2 2.921(8), P1–N2 1.580(3), P2–N2 1.584(3), C1–Au–C2 179.0(2), P1–N2–P2 136.4(2).

3.2. Crystal structure descriptions

Compound **1** contains a linear coordinated Au(I) ion, by cyanide and phenylacetylide, with Au–C distances of 1.97 and 1.99 Å and the C–Au–C angle being 179.0°. The geometric parameters are similar to those of the neutral Au(I) complex [PhC≡C–Au–C_{carbene}] (C_{carbene} = 1,3-diisopropylbenzimidazol-2-ylidene; Au–C distance: 1.99, C–Au–C angle: 177.0°) [24]. There are no close contacts between the cation and the anion in compound **1**. The N atom of the coordinated cyanide ligand, accepts a H bond from a lattice water (N...O distance: 3.01 Å, N–H–O angle: 155°). The other water hydrogen forms a H bond to a lattice acetone (O...O distance: 2.92 Å, O–H–O angle: 173°). The intramolecular bonds for the PPN cation are uneventful. A full list of bond lengths and angles is to be found in Table S1. A projection of compound **1** is presented in Fig. 1.

Compound **2** also contains a linear coordinated Au(I) ion, by cyanide and *t*-butylacetylide. The Au(I) ion and the *t*-butylacetylido ligand are disordered over two positions with occupancies of 65% and 35%. There are no close contacts between the cation and the anion. The N atom of the coordinated cyanide ligand, accepts an H bond from a lattice water (N...O distance: 2.90 Å, N–H–O angle: 177°). The disorder of the AuCCMe₃ unit is illustrated in Fig. S1. A list of bond lengths and angles is to be found in Table S2. A projection of the asymmetric unit displaying the main component of compound **2** is given in Fig. 2.

Packing in both compounds is uneventful, and packing diagrams for both compounds are presented in Figs. S2 and S3.

3.3. Luminescence studies

The emission and excitation spectra of compounds **1** and **2** were studied in the solid state and compared with earlier data from our laboratory on related compounds [15–17]. It appears that the moderate intense luminescence observed for the phenylacetylide compound (compound **1**) is weaker than that of related bis(cyanide)silver and copper compounds. More surprising is the

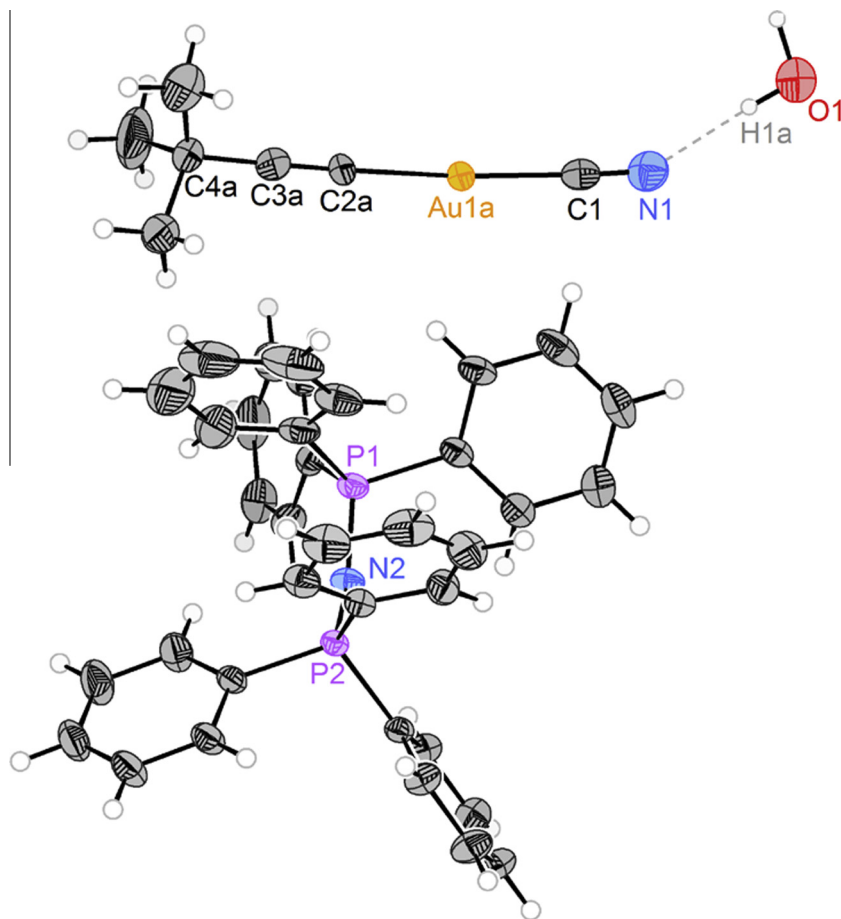


Fig. 2. Projection of cation, anion and lattice solvent molecules in compound **2** with thermal ellipsoid plot at the 50% levels of probability. Only the main component (65% occupancy) of the disordered part is depicted. Selected bond lengths [Å] and angles [°] are: Au1a–C1 2.003(4), Au1a–C2a 2.013(8), C1–N1 1.122(5), C2a–C3a 1.199(12), C3a–C4a 1.465(11), N1···O1 2.900(8), P1–N2 1.582(2), P2–N2 1.586(2), C1–Au1a–C2a 174.6(3), P1–N2–P2 135.29(17).

fact that the *t*-butylacetylide compound (compound **2**) shows hardly any luminescence at all. The spectra for compound **1** are displayed in Figs. 3 and 4. Apparently, the aromatic versus aliphatic structure of the ligand around Au has a dramatic effect on the emission behavior. As both compounds are homogeneous crystal-

line powders, we have no reasons to assume that the (non) luminescence is related to crystal impurities. This difference, of course invites to further investigation, and currently we are investigating other aromatic and aliphatic acetylides, also as free ligands and a change of the metal ion to Ag(I).

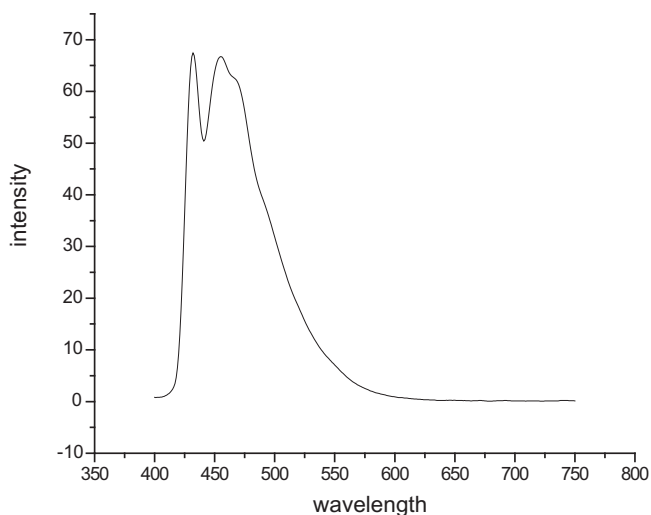


Fig. 3. Emission spectrum of compound **1** (excited at 310 nm).

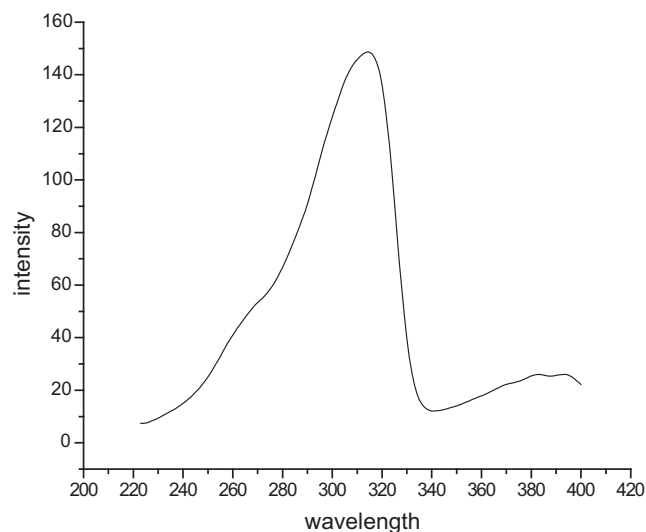


Fig. 4. Excitation spectrum of compound **1** (monitored at 431 nm).

4. Concluding remarks

The results presented above have shown that cyanide ligands in Au(I) compounds can be replaced by acetylide ligands. The large counteranion PPN remains innocent in the formed compounds and has no short intermolecular contacts in the solid state. Open spaces in the lattice are filled with water and – in the case of compound **1** – also with acetone. The water donates a hydrogen bond to the coordinated C≡N in both cases, and in case of compound **1** also a hydrogen bond is donated to lattice acetone.

The luminescence difference between compounds **1** and **2** in the solid state is not yet understood; it might be related to a quenching in the lattice in the case of the *t*-butyl group, where luminescence is absent.

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Appendix A. Supplementary data

CCDC 1030371 and 1030372 contains the supplementary crystallographic data for compounds **1** and **2**. 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. Supplementary data associated with this article can be found, in the online version, at <http://dx.doi.org/10.1016/j.poly.2014.12.022>.

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