ISSN 1070-3284, Russian Journal of Coordination Chemistry, 2024, Vol. 50, No. 1, pp. 40–48. © Pleiades Publishing, Ltd., 2024.

To the 300th year anniversary of the foundation of the Saint Petersburg State University

Gold(I) Chloride Complexes with 4-Halo-Substituted Phenyl Isocyanide Ligands

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Received April 5, 2023; revised April 10, 2023; accepted April 10, 2023

Abstract—A series of gold(I) monoisocyanide [AuCl(CNC_6H_4-4-X)] (X = Cl (**IIa**), Br (**IIb**), I (**IIc**) and bis-isocyanide [Au(CNC_6H_4-4-X$)_2$](PF_6) (X = Cl (**IIIa**), Br (**IIIb**), I (**IIIc**) complexes were prepared by the reaction of [AuCl(Tht)] (Tht = tetrahydrothiophene) with the specified isocyanide. The molecular structure of **IIa**–**IIc** was established by X-ray diffraction (CCDC no. 2253450 (**IIa**), 2253447 (**IIb**), 2253448 (**IIc**)). The crystals of **IIb** and **IIc** are isostructural; they were found to have several types of intermolecular interactions, particularly, C–X···Cl–Au halogen bonds, π-hole (C_{CNR})···d_{z^2}(Au) interactions, and Au···Au aurophilic contacts, which form together a two-layer 2D supramolecular polymer. The crystals of **IIb**, **IIc** and **IIIa**, **IIIb** exhibit phosphorescence at room temperature; compounds **IIa** and **IIIc** do not possess luminescent properties; and mechanical grinding of **IIa**–**IIc** and **IIIa**–**IIIc** powders does not change the photophysical properties.

Keywords: photoluminescence, gold complexes, isocyanides, non-covalent interactions

DOI: 10.1134/S1070328423600596

INTRODUCTION

The coordination compounds of gold are in-demand for the design of functional materials and medicinal products. The large diversity of photophysical properties inherent in gold complexes has made this class of compounds a highly promising type of metal-containing luminophores [1–6]. Luminescent gold complexes are used as emission layers in organic light-emitting diodes [1, 7, 8], luminescent chemosensors in analytical chemistry [1], and photochromic compounds in optoelectronic materials [9–11] and organic data storage devices [12]. The photophysical properties of gold complexes are mainly determined by properties of the organic ligand; however, in the solid-phase, the photophysical properties are also related to intermolecular non-covalent interactions [13]. In particular, they are substantially affected by the intermolecular Au···Au aurophilic contacts, which are a special case of metal–metal non-covalent interactions [14–16].

Gold(I) complexes with isocyanide ligands have been actively studied in the last decade [17]. Owing to the linear configuration of the isocyanide moiety, most of the investigated compounds have short Au···Au contacts in the solid phase; the variation of the isocyanide substituent promotes the formation of various supramolecular aggregates: dimers [18], tetramers [19], and 1D- [20] and 2D-polymers [21–28]. Extensive use of gold(I) isocyanides in the design of materials is prevented by the uncontrolled change in the photophysical characteristics due to the formation of several crystal forms [29], since different crystalline phases have different photophysical properties [20]. The introduction of additional non-covalent binding sites into organic ligands may stabilize a particular crystal form via structure-determining non-covalent interactions and thus solve the problem of production of materials with reproducible photophysical characteristics [30–34].

In recent studies, we proposed a new class of organometallic synthons for crystal chemical design involving halogen bonds, particularly, palladium(II) and platinum(II) complexes with halogen-substituted phenyl isocyanides [M($X^M$$)_2$($CNC_6H_4$-4-X)L] (M = Pd, Pt; X^M = Br, I; X = Cl, Br, I; L = CNC_6H_4-4-X, PPh_3) [35–37]. In a series of experimental and theoretical studies, we demonstrated that the covalently bound halogen atoms in the aryl isocyanide ligands have an electrophilic region with a positive molecular electrostatic potential corresponding to a σ-hole site [38], which makes these halogen atoms potential halogen bond donors [36]. Meanwhile, the X^M halides bound to the metal center have a negative molecular electrostatic potential over the whole surface and can act exclusively as nucleophilic components in the halogen bond formation. We assumed that crystals of gold(I) chloride complexes with 4-halogen-substituted phenyl isocyanide ligands can be stabilized via the formation of an intermolecular halogen bond, since these compounds contain both electrophilic and nucleophilic sites for non-covalent interactions.

In this study, we obtained a series of gold(I) monoisocyanide [AuCl(CNC$_6$H$_4$-4-X)] (X = Cl, **IIa**; Br, **IIb**; I, **IIc**) and bis-isocyanide [Au(CNC$_6$H$_4$-4-X)$_2$](PF6)) (X = Cl, **IIIa**; Br, **IIIb**; I, **IIIc**) complexes with 4-halogen-substituted phenyl isocyanide ligands and studied their crystal structure, photophysical properties in the solid state (luminescence, excited state lifetime, and photoluminescence quantum yield), and the effect of mechanical stimulus on the luminescent properties in the solid state.

EXPERIMENTAL

The commercial starting compounds and solvents (Aldrich) were used in this study as received. Elemental analysis (C,H,N) was carried out on a Euro EA3028-HT elemental analyzer. Electrospray ionization mass-spectrometric analysis was performed on a Bruker micrOTOF spectrometer (Bruker Daltonics). Methanol was used as the solvent. The *m/z* values are given for signals of the most abundant isotopologues. Infrared spectra were measured on a Shimadzu FTIR 8400S spectrometer (4000–400 cm^{-1}; samples were prepared as KBr pellets). ^{1}H and ^{13}C{^{1}H} NMR spectra were measured in solution on a Bruker Avance II+ spectrometer (operating at 400.13 MHz (^{1}H), 100.61 MHz (^{13}C)) at room temperature; CDCl$_3$ was used as the solvent.

Synthesis of complexes IIa–IIc. A solution of isocyanide (CNR) (0.16 mmol) in CH_2Cl_2 (2 mL) was added dropwise at room temperature to a solution of [AuCl(Tht)] (**I**) (50 mg, 0.16 mmol) in CH_2Cl_2 (2 mL). The reaction mixture was stirred at room temperature for 20 min and then evaporated to dryness under reduced pressure. The solid product was washed with hexane (2 mL), crystallized from a CH_2Cl_2–hexane mixture (4 mL, 3 : 1 v/v), and dried in air.

The yield of **IIa** was 48 mg (98%). White powder.

For $C_7H_4NCl_2Au$

Anal. calcd., %	C, 22.72	H, 1.09	N, 3.79
Found, %	C, 22.93	H, 1.11	N, 3.68

MS, *m/z*: for $C_7H_4NCl_2AuNa^+$, calcd. 391.9284, found [M + Na]$^+$ 391.9289. IR (KBr; ν, cm^{-1}): 2236 ν(C≡N). ^{1}H NMR (CDCl$_3$, δ, ppm): 7.50–7.56 (m, 4H). ^{13}C{^{1}H} NMR (125.73 MHz, CDCl$_3$): 122.90 (C$_{\rm CNR}$), 128.17 (C^3 and C^5), 130.52 (C^2 and C^6), 138.27 (C^4). The C^1 signal could not be detected due to the poor solubility of the sample.

The yield of **IIb** was 47 mg (97%). White powder.

For $C_7H_4NClBrAu$

Anal. calcd., %	C, 20.29	H, 0.97	N, 3.38
Found, %	C, 20.64	H, 1.12	N, 3.22

MS, *m/z*: for $C_7H_4NAuBrClNa^+$, calcd. 435.8779, found [M + Na]$^+$ 435.8778. IR (KBr; ν, cm^{-1}): 2225 ν(C≡N). ^{1}H NMR (400.13 MHz, CDCl$_3$, δ, ppm): 7.44 (d, 2H, $^3J_{\rm H,H}$ = 8.7 Hz), 7.66–7.70 (m, 2H). ^{13}C{^{1}H} NMR (125.73 MHz, CDCl$_3$, δ, ppm): 126.43 (C^4), 128.23 (C^3 and C^5), 133.51 (C^2 and C^6). The C^1 and C$_{\rm CNR}$ signals could not be detected due to the poor solubility of the sample.

The yield of **IIc** was 48 mg (93%). Light yellow powder.

For $C_7H_4NClIAu$

Anal. calcd., %	C, 18.22	H, 0.87	N, 3.04
Found, %	C, 18.83	H, 0.90	N, 2.95

MS, *m/z*: calcd. for $C_7H_4NAuClINa^+$, calcd. 483.8640, found [M + Na]$^+$ 483.8640. IR (KBr; ν, cm^{-1}): 2225 ν(C≡N). ^{1}H NMR (400.13 MHz, CDCl$_3$, δ, ppm): 7.27–7.31 (m, 2H), 7.89–7.93 (m, 2H). ^{13}C{^{1}H} NMR (100.61 MHz, $(CD_3)_2CO/CH_2Br_2$, δ, ppm): 98.24 (C^4), 128.77 (C^3 and C^5), 139.36 (C^2 and C^6). The C^1 and C$_{\rm CNR}$ signals could not be detected due to the poor solubility of the sample.

Synthesis of complexes IIIa–**IIIc**. A solution of KPF_6 (0.50 mmol, 90 mg) in MeOH (2 mL) was added to a solution of [AuCl(Tht)] (**I**) (50 mg, 0.16 mmol) in CH_2Cl_2 (2 mL), and then a solution of CNR (0.32 mmol) in CH_2Cl_2 (2 mL) was added dropwise at room temperature. The reaction mixture was stirred at room temperature for 30 min, then the precipitate was separated by decantation, and the decantate was filtered through celite on a porous glass filter. The filtrate was evaporated to dryness on a rotary evaporator; and the solid product was crystallized from a CH_2Cl_2–hexane mixture (4 mL, 3 : 1 v/v).

The yield of **IIIa** was 41 mg (81%). Light yellow powder.

For $C_{14}H_8N_2Cl_2F_6PAu$

Anal. calcd., %	C, 27.25	H, 1.31	N, 4.54
Found, %	C, 27.33	H, 1.45	N, 4.48

MS, *m/z*: for $C_{14}H_8N_2AuCl_2^+$, cacld. 470.9725; found $[M]^+$ 470.9719. IR (KBr; ν, cm^{-1}): 2238 ν(C≡N). ^1H NMR (400.13 MHz, $CDCl_3$, δ, ppm): 7.37–7.41 (m, 4H), 7.43–7.47 (m, 4H). $^{13}C\{^1H\}$ NMR (125.73 MHz, $CDCl_3$, δ, ppm): 124.49 (C^3 and C^5), 129.51 (C^2 and C^6), 133.86 (C^4). The C^1 and C_{CNR} signals could not be detected due to the poor solubility of the sample.

The yield of **IIIb** was 42 mg (83%). White powder.

For $C_{14}H_8N_2F_6PBr_2Au$

Anal. calcd., %	C, 23.82	H, 1.14	N, 3.97
Found, %	C, 24.04	H, 1.12	N, 3.91

MS, *m/z*: for $C_{14}H_8N_2AuBr_2^+$, calcd. 558.8720, found $[M]^+$ 558.8718. IR (KBr; ν, cm^{-1}): 2231 ν(C≡N). ^1H NMR (400.13 MHz, $CDCl_3$, δ, ppm): 7.38 (d, 4H, $^3J_{H,H}$ = 8.9 Hz), 7.54 (d, 4H, $^3J_{H,H}$ = 8.9 Hz). $^{13}C\{^1H\}$ NMR (125.73 MHz, $CDCl_3$, δ, ppm): 124.71 (C^3 and C^5), 132.50 (C^2 and C^6). The C^1, C^4, and $C_{isocyanide}$ signals could not be detected due to the poor solubility of the sample.

The yield of **IIIc** was 35 mg (70%). Light yellow powder.

For $C_{14}H_8N_2F_6PI_2Au$

Anal. calcd., %	C, 21.02	H, 1.01	N, 3.50
Found, %	C, 20.86	H, 0.91	N, 2.91

MS, *m/z*: for $C_{14}H_8N_2AuI_2^+$, calcd. 654.8442; found $[M]^+$ 654.8442. IR (KBr; ν, cm^{-1}): 2224 ν(C≡N). ^1H NMR (400.13 MHz, $CDCl_3$, δ, ppm): 7.33 (d, 4H, $^3J_{H,H}$ = 8.5 Hz), 7.74 (d, 4H, $^3J_{H,H}$ = 8.5 Hz). $^{13}C\{^1H\}$ NMR (125.73 MHz, $CDCl_3$, δ, ppm): 125.34 (C^3 and C^5), 138.69 (C^2 and C^6). The C^1, C^4, and $C_{isocyanide}$ signals could not be detected due to the poor solubility of the sample.

The single crystals of compounds **IIa**–**IIc** were obtained by slow evaporation of the solvent from solutions of the complexes in dichloromethane.

X-ray diffraction study of **IIa**, **IIb**, and **IIc** was carried out on a Xcalibur, Eos diffractometer (monochromatic CuK_α radiation, λ = 1.54184 Å) at 100 K. The structure was solved by the direct methods and refined using the SHELX program [39] embedded in the OLEX2 package [40]. The absorption correction was applied empirically using the CrysAlisPro software with spherical harmonics implemented in the SCALE3 ABSPACK scaling algorithm [41]. The hydrogen atoms were refined in the calculated positions.

The structures were deposited with the Cambridge Crystallographic Data Centre (CCDC nos. 2253450 (**IIa**), 2253447 (**IIb**), and 2253448 (**IIc**)); additional crystallographic data are available at www.ccdc.cam.ac.uk/data_request/cif.

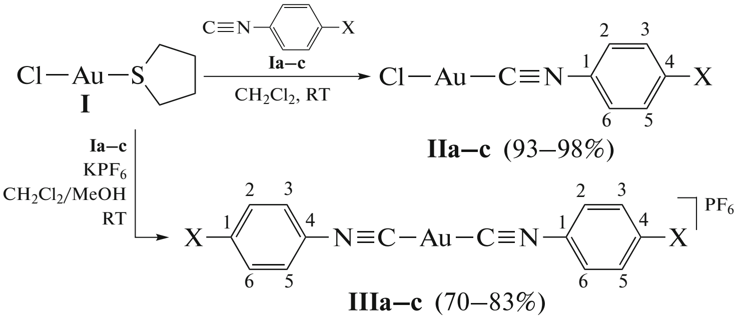
IIa. $C_7H_4NCl_2Au$, M = 369.98, monoclinic, space group $P2_1/m$, a = 4.9552(2), b = 7.4712(2), c = 11.4845(3) Å, β = 94.729(2)°, V = 423.72(2) $Å^3$, Z = 2, ρ(calcd.) = 2.900 g/cm^3, μ = 37.848 mm^{-1}, 0.21 × 0.15 × 0.14 mm^3 crystal size; a total of 3196 reflections, 817 unique reflections with $I > 2\sigma(I)$ (R_{int} = 0.0508), $R_1(|F_o| \geq 4\sigma F)/R_1$ (all data) 0.0369/0.0983, $wR_2(|F_o| \geq 4\sigma F)/wR_2$ (all data) 0.0375/0.0992, ρ_{min}/ρ_{max} = 2.81/–2.02e/$Å^3$.

IIb. $C_7H_4NClBrAu$, M = 414.44, monoclinic, space group $P2_1/c$, a = 8.8202(2), b = 11.6797(4), c = 15.6346(5) Å, β = 94.573(3)°, V = 865.63(6) $Å^3$, Z = 4, ρ(calcd.) = 3.180 g/cm^3, μ = 39.622 mm^{-1}, 0.12 × 0.08 × 0.05 mm^3 crystal size, a total of 7182 reflections, 1514 unique reflections with $I > 2\sigma(I)$ (R_{int} = 0.0741), $R_1(|F_o| \geq 4\sigma F)/R_1$ (all data) 0.0349/0.0909, $wR_2(|F_o| \geq 4\sigma F)/wR_2$ (all data) 0.0382/0.0934, ρ_{min}/ρ_{max} = 1.10/–1.76 e/$Å^3$.

IIc. $C_7H_4NClIAu$, M = 461.43, monoclinic, space group $P2_1/c$, a = 4.0864(2), b = 16.1494(5), c = 13.8148(4) Å, β = 96.679(3)°, V = 905.49(6) $Å^3$, Z = 4, ρ(calcd.) = 3.385 g/cm^3, μ = 59.479 mm^{-1}, 0.09 × 0.05 × 0.03 mm^3 crystal size, a total of 7073 reflections, 1590 unique reflections with $I > 2\sigma(I)$ (R_{int} = 0.0588), $R_1(|F_o| \geq 4\sigma F)/R_1$ (all data) 0.0317/0.0811, $wR_2(|F_o| \geq 4\sigma F)/wR_2$ (all data) 0.0346/0.0829, ρ_{min}/ρ_{max} = 1.62/–1.34 e/$Å^3$.

RESULTS AND DISCUSSION

Compounds **IIa**–**IIc** were synthesized by the reactions of the precursor [AuCl(Tht)] (**I**, Tht = tetrahydrothiophene) with a stoichiometric amount of specified isocyanide (**Ia**–**c**) in CH_2Cl_2 at room temperature; the yields of the target compounds after recrystallization were 93–98%. Complexes **IIIa**–**IIIc** were obtained by the reactions of **I** with two equivalents of isocyanide (**Ia**–**c**) in the presence of four equivalents of KPF_6 (70–83% yield). The synthetic routes to **IIa**–**IIc** and **IIIa**–**IIIc** are depicted in Scheme 1.



X = Cl (a), Br (b), I (c)

Scheme 1.

Compounds were isolated as colorless (**IIa**–**IIb**, **IIIb**) or light yellow (**IIc**, **IIIa**, **IIIc**) finely crystalline powders and identified by elemental analysis ESI MS, IR spectroscopy, and ^{1}H and ^{13}C{^{1}H} NMR spectroscopy. The structures of **IIa**–**IIc** in the solid state were additionally confirmed by single-crystal X-ray diffraction. Compound **IIc** was obtained previously as an intermediate [42, 43]; however its crystal structure has not been stidied; compounds **IIa**, **IIb** and **IIIa**–**IIIc** have not been reported previously.

The mass spectra of complexes **IIa**–**IIc** and **IIIa**–**IIIc** contain peaks for $[M + Na]^+$ (**IIa**–**IIc**) and $[M-PF_6]^+$ (**IIIa**–**IIIc**) ions; the peaks have a characteristic isotopic distribution unambiguously indicating the content of halogen atoms in the ions corresponding to the assumed structure. The IR spectra of **IIa**–**IIc** and **IIIa**–**IIIc** show one intense absorption band at 2214–2238 cm^{-1} for C≡N stretching mode. The ν(CN) maximum in the spectra of **IIa**–**IIc** and **IIIa**–**IIIc** are shifted by 90–112 cm^{-1} to higher frequency relative to the spectra of uncoordinated isocyanides (ν(CN) = 2125–2228 cm^{-1} [44]); this attests to increasing electrophilicity of the isocyanide carbon atom upon coordination, which is typical of late transition metal complexes [45]. In all cases, the ^{1}H and ^{13}C{^{1}H} NMR spectra contain single sets of signals, indicating the existence of these complexes in solutions as only one type of species. The isocyanide coordination to the gold atom is accompanied by a pronounced downfield shift of the signal for the terminal carbon atom in the ^{13}C{^{1}H} NMR spectrum (for CNR, δ_C is 165–169 ppm; for **IIa**, δ_C is 122.9 ppm), which is also the case for other similar isocyanide complexes [46].

The molecular structures of **IIa**–**IIc** were confirmede by single crystal X-ray diffraction analysis (Figs. 1–3). Selected bond lengths and bond angles are summarized in Table 1.

The metal center in **IIa**–**IIc** has a linear geometry of the ligand environment, being bound to chlorine and carbon atoms (the ClAuC angle is 178°). The Au–C distance is 1.918(10)–1.923(9) Å, which is typical of isocyanide complexes [47]. The Au–C–N–C groups are nearly linear, the CN bond lengths in the isocyanide moieties are similar to the lengths of analogous bonds in other isocyanide complexes.

In the structure of **IIa**, the distances between the gold atoms are 3.8411(19) Å, which is greater than twice the gold van der Waals radius (R_{vdW}) proposed by Bondi ($2R_{vdW}$(Au) = 3.32 Å [48], $r_{Au,Au} = d(Au\cdots Au)/2R_{vdW}(Au) = 1.16$). Meanwhile, this distance is shorter than twice the Alvarez van der Waals radius of gold ($2R_{vdW}$(Au) = 4.64 Å [49], $r_{Au,Au} = 0.76$). Thus, most likely, the structure of **IIa** has weak aurophilic interactions. However, an unambiguous conclusion can be drawn only from quantum chemical calculations. Also, there are weak hydrogen bonds in **IIa** between the aryl hydrogen atom and the chloride ligand (C(3)–H···Cl) = 2.833 Å) (Fig. 3).

The crystals of compounds **IIb** and **IIc** proved to be isostructural, demonstrating Br/I isomorphism [24]. Several types of intermolecular interactions were identified, particularly (a) C–X···Cl–Au halogen bonds, (b) π-hole (C_{CNR})···d_{z^2}(Au) interactions, and (c) aurophilic Au···Au interactions (Fig. 3).

The length of the C–X···Cl–Au contacts (X = Br, I) between the halogen substituent in the benzene ring and the chloride ligand (Br(1)···Cl(1) = 3.48712(12) Å, $r_{Br,Cl} = 0.97$ for **IIIb**, I(1)···Cl(1) = 3.53555(9) Å, $r_{I,Cl} = 0.96$ for **IIIc**) is smaller than the sum of the van der Waals radii, and the C–X···Cl angle is close to 180° (158.1(2)° for **IIIb** and 157.4628(9)° for **IIIc**), which complies with the IUPAC geometric criteria for a halogen bond [50]; the halogen atom X is the halogen bond donor, while the chloride ligand, a nucleophilic partner, is the halogen bond acceptor. The extended C–X···Cl–Au halogen bonds form a 1D-supramolecular polymer. Note that the formation of supramolecular 1D- and 2D-polymers via halogen

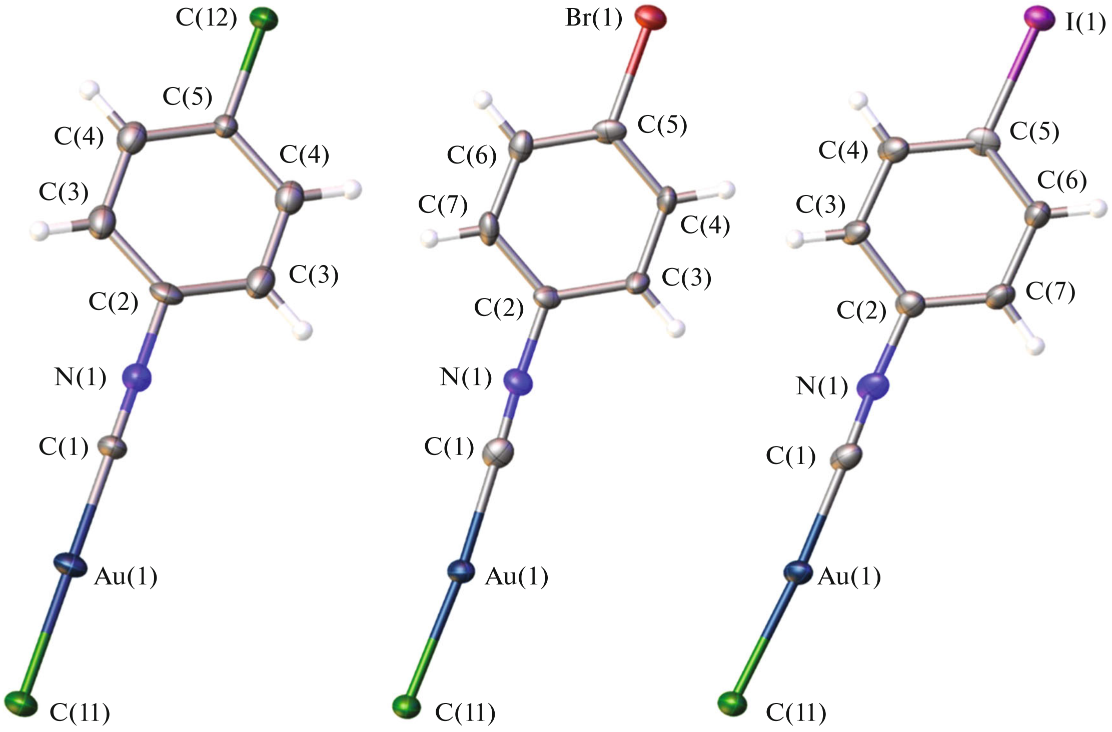


Fig. 1. Structures of complexes (left) **IIa**, (middle) **IIb**, and (right) **IIc**, according to X-ray diffraction data with atom numbering.

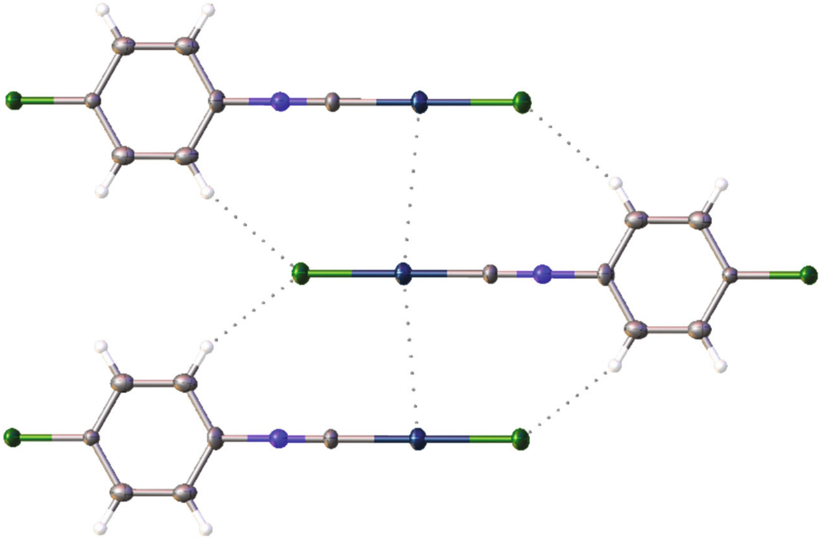


Fig. 2. Intermolecular interactions in **IIa**.

bonds was reported previously for palladium(II) and platinum(II) complexes with halogen-substituted aryl isocyanides $[MX^1_2(CNC_6H_4\text{-}4\text{-}X^2)_2]$ (M = Pd, Pt; X^1, X^2 = Cl, Br, I) [35, 37]. The absence of halogen bonds in structure **IIa** and their presence in structures **IIb**–**IIc** may be attributable to the increase in the halogen atom polarizability in isocyanides in the series 4-chlorophenyl isocyanide–4-bromophenyl isocyanide–4-iodophenyl isocyanide and, as a consequence, to the ability to form intermolecular halogen bonds [51].

Short C1···Au(1) contacts were identified between 1D layers; they can be interpreted as π-hole

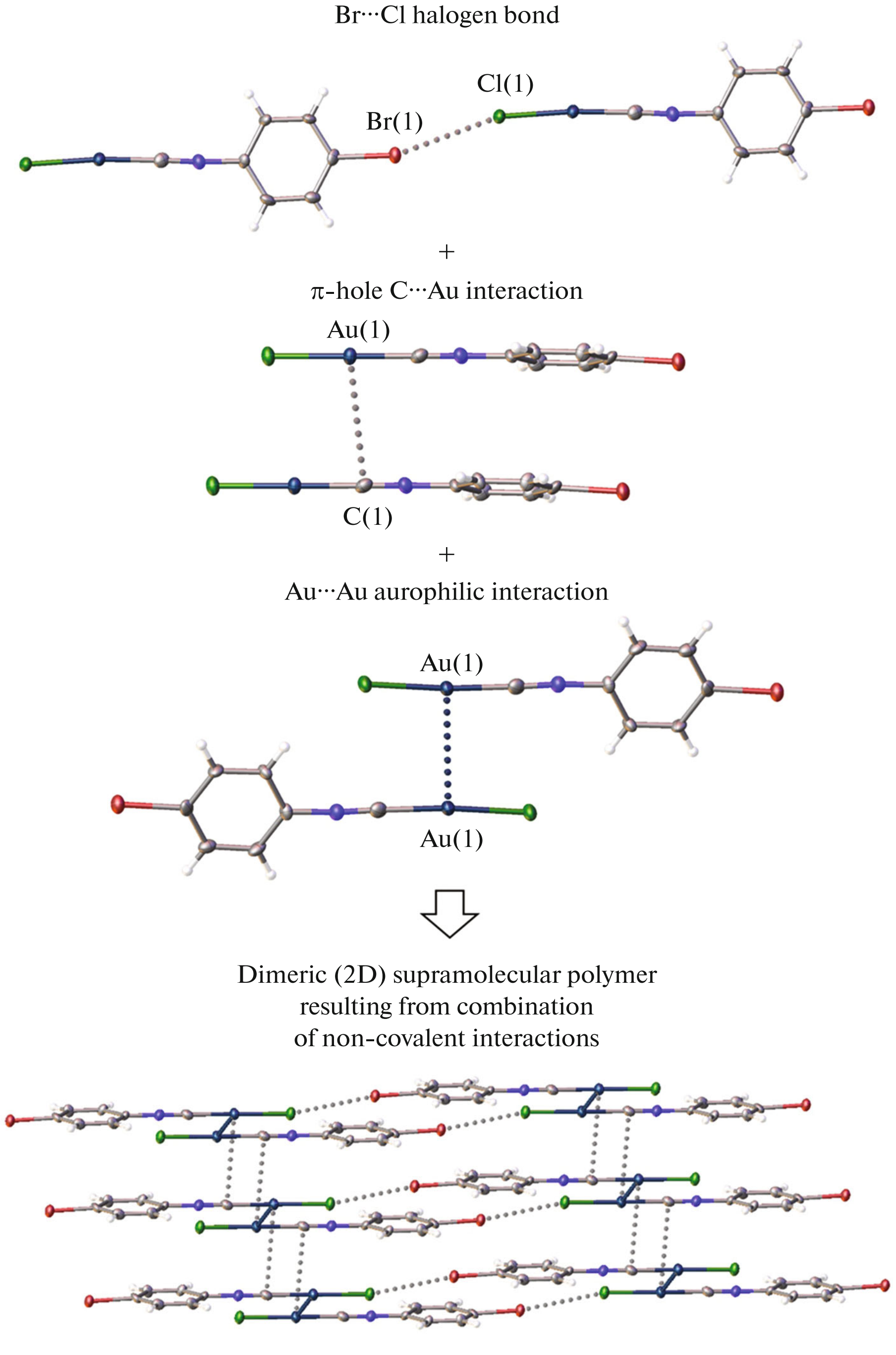


Fig. 3. Two-layer 2D supramolecular architecture of **IIb** formed due to combination of non-covalent interactions. Crystals of **IIc** have a similar supramolecular structure with similar non-covalent interactions.

$(\mathrm{C1_{CNR}})\cdots d_{z^2}(\mathrm{Au1})$ interactions between the gold d_{z^2}-orbital and the π-hole of the isocyanide moiety [52, 53], the (C1···Au1) distance (3.530–3.618 Å) is shorter than the sum of the Alvarez van der Waals radii ($R_{\mathrm{vdW}}(\mathrm{N}) + R_{\mathrm{vdW}}(\mathrm{Au}) = 3.98$ Å, $r_{\mathrm{N,Au}} = 0.88$). In the supramolecular dimer, the Au(1)···Au(1) distance between two neighboring molecules is shorter than twice the gold van der Waals radius according to Bondi (3.2659(6) and 3.2793(8) Å for **IIIb** and **IIIc**, respectively, $r_{\mathrm{Au,Au}} = 0.98$); hence, the Au(1)···Au(1) contact can be classified as an aurophilic interaction [29, 41–43]. The combination of the identified contacts in **IIIb** and **IIIc** gives rise to a bilayer 2D supramolecular polymer (Fig. 3).

Table 1. Selected bond lengths (Å) and bond angles (deg) for **IIa**–**IIc**

Bond	**IIa**	**IIb**	**IIc**
		d, Å	
Au(1)–Cl(1)	2.259(3)	2.267(2)	2.2611(17)
Au(1)–C(1)	1.918(10)	1.923(9)	1.920(8)
C(1)–N(1)	1.150(14)	1.150(12)	1.163(11)
N(1)–C(2)	1.403(13)	1.392(10)	1.392(10)
Angle		ω, deg	
Cl(1)Au(1)C(1)	179.7(3)	175.2(3)	175.7(2)
Au(1)C(1)N(1)	177.7(9)	178.4(8)	178.0(8)
C(1)N(1)C(2)	179.9(10)	176.5(8)	176.3(8)

On exposure to UV radiation (360 nm), the crystals of compounds **IIIb**, **IIIc** and **IIIa**, **IIIc** exhibit visually detectable luminescence at room temperature (Fig. 4). Compounds **IIa** and **IIIc** do not show luminescence, like solutions of all of these compounds in dichloromethane. The large Stokes shift and the long lifetime of the excited state in the microsecond range imply a triplet nature of luminescence for these complexes,

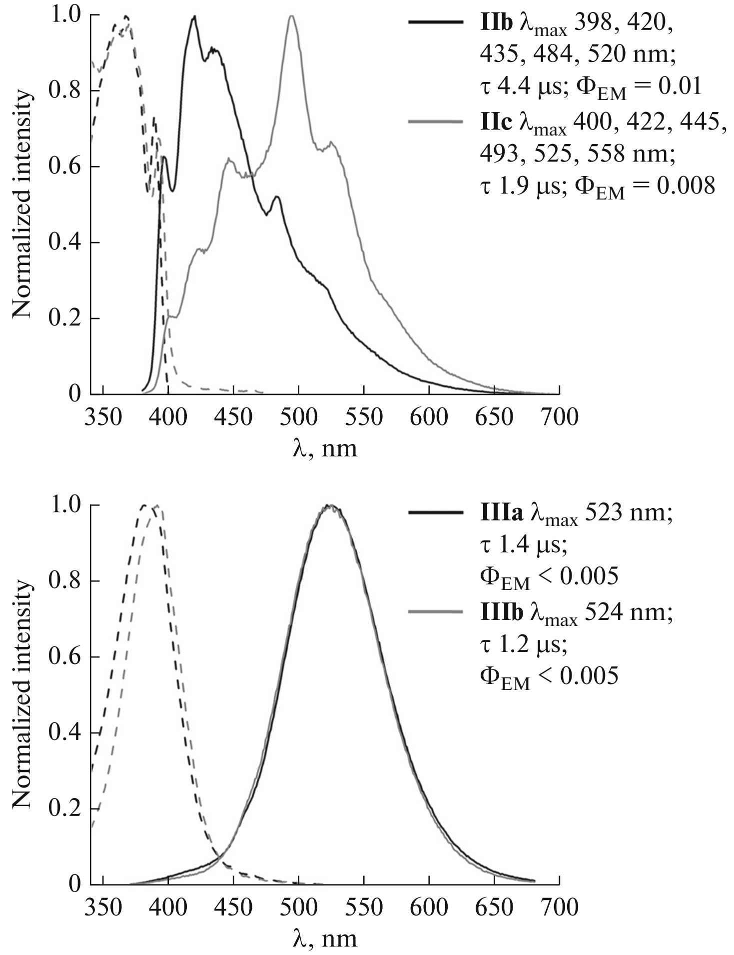


Fig. 4. Normalized (dashed line) excitation and (solid line) luminescence spectra for crystalline samples of **IIb**, **IIc** and **IIIa**, **IIIb** at 298 K.

i.e., phosphorescence. Considering the published data on the luminescence of gold(I) isocyanide complexes [54–60], one can conclude that isocyanide orbitals make a significant contribution to the radiative excited state of **IIb** and **IIc**, and emission is related to the intraligand ^{3}IL (CNR) transitions including ^{3}MLCT transitions. The non-structured luminescence spectrum for bis-isocyanide complexes **IIIa**, **IIIb** is probably related to the excimer radiation produced by aurophilic and/or π–π interactions existing in the solid phase [55, 59, 61]. Long-term grinding of crystals **IIa**–**IIc** and **IIIa**–**IIIc** in a mortar does not induce a visible change in the sample color or photoluminescence color, which indicates the absence of mechanoluminescent properties.

Thus, we studied a series of gold(I) monoisocyanide [AuCl(CNC_6H_4-4-X)] and bis-isocyanide [Au(CNC_6H_4-4-X)$_2$](PF_6) complexes with 4-halogen-substituted phenyl isocyanide ligands. The crystals of [AuCl(CNC_6H_4-4-Br)] (**IIb**) and [AuCl(CNC_6H_4-4-I)] (**IIc**) proved to be isostructural, being an example of Br/I isomorphism; several types of intermolecular interactions have been identified in these compounds, particularly, (a) C–X···Cl–Au halogen bonds, (b) π-hole (C_{CNR})···d_{z^2}(Au) interactions, and (c) Au···Au aurophilic interactions; the combined action of these factors gives rise to a two-layer 2D supramolecular polymer. The crystals of **IIb**, **IIc**, **IIIa**, and **IIIb** exhibit phosphorescence at room temperature; compounds **IIa** and **IIIc** possess no luminescent properties; mechanical grinding of **IIa**–**IIc** and **IIIa**–**IIIc** powders does not induce changes in their photophysical properties.

ACKNOWLEDGMENTS

This study was carried out using research equipment of the resource centers of the Saint Petersburg State University: Magnetic Resonance Investigation Methods; X-ray Diffraction Investigation Methods; Methods of Analysis of the Compound Composition; Educational Center in Chemistry; Optical and Laser Methods of Investigation of Matter; Center for Diagnostics of Functional Materials for Medicine, Pharmacology, and Nanoelectronics; and Cryogenic Department and Computer Center. The authors are grateful to A.S. Ketova for conducting test experiments in the initial stages of the study. The authors wifh to thank Yu.R. Shakirova for valuable comments and useful discussion.

FUNDING

This study was supported by the Russian Science Foundation (no. 21-73-10083).

CONFLICT OF INTEREST

The authors of this work declare that they have no conflicts of interest.

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Translated by Z. Svitanko