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ЗАКОНОМЕРНОСТИ РАСПРЕДЕЛЕНИЯ ПРОСТЫХ ВЕЩЕСТВ И ХИМИЧЕСКИХ СОЕДИНЕНИЙ ПО ТЕМПЕРАТУРАМ ПЛАВЛЕНИЯ И КИПЕНИЯ И ИХ ВЗАИМОСВЯЗЬ С ДРУГИМИ ФИЗИКО-ХИМИЧЕСКИМИ ПАРАМЕТРАМИ

Исследованы в большой выборке (более 2770 объектов) закономерности взаимосвязи между температурами плавления ($T_П$) и кипения ($T_К$) простых веществ (химических элементов) и различных химических соединений как неорганической, так и органической природы. Выявлены корреляции параметров соотношений температур с мольными объемами (V_E) и удельной плотностью (d_E) для 118 известных сегодня химических элементов. Выявлены строгие формульные связи с другими физико-химическими параметрами и константами. Удалось спрогнозировать и уточнить $T_П$, $T_К$, V_E и d_E химических элементов всего трансуранового ряда.

Ключевые слова: температуры плавления и кипения, химические элементы и соединения, мольный объем, плотность, константа гравитации, постоянная тонкой структуры, трансурановые элементы, предел массы атома.

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REGULARITIES OF DISTRIBUTION BY MELTING AND BOILING POINT OF SIMPLE SUBSTANCES AND CHEMICAL COMPOUNDS AND THEIR RELATIONSHIP WITH OTHER PHYSICAL AND CHEMICAL PARAMETERS

Investigated in large sample (over 2770 objects) the patterns of relationship between melting points (T_M) and boiling point (T_B) of simple substances (chemical elements) and different chemical compounds, inorganic and organic nature. The detected temperature ratio parameter to correlation with amount of molar volume (V_E) and specific density (d_E) for the 118 today known elements. Found the strict formula mating with other physical-chemical parameters and constants. Able to predict and refine T_M, T_B, V_E and d_E of the chemical elements all Tran's uranium series.

It is show that the correlation equations of lines of distribution of simple substances (chemical) compounds of organic and inorganic nature in the form of functions: $T_M = f(\triangle T_{MB})$, $T_B = f(\triangle T_{MB})$, where $\triangle T_{MB} = (T_B - T_M)$, and the boundaries of their special zones clearly correlated to the level of simple mathematical formulas with the fundamental constants. In particular next constant: the fine structure ($\alpha_0 = 0.0072973524$; constant of gravitation ($G = 6,67428 \times 10^{-11}$ $m^3 \cdot (c \cdot kg)^{-2}$; the electric impedance ($Z_0 = c\mu_0 = 376,73031$); a molar volume ($V_0 = 0.0224139682$ $m^3 \cdot k \cdot mol^{-1}$; a specific energy chemical connection $\triangle Go = 395458,1716$ $J \cdot mol^{-1}$; and gravity radius (equally weighted according to Kepler's laws) $r_\oplus = 1467,584624$ m, and others.

It is also shown that areas of selected points (T_i) on the function of the $T_M = f(\triangle T_{MB})$, for which $T_M = T_i$, the approximation lines on the function of $T_B = f(\triangle T_{MB})$, are linear in nature. This lines have characteristic coefficients: $y = 1,00092660467x + 302,179177315$, and tangent of an angle whose angle to the axis of the horizontal axis $tg(\alpha)_K = 1,0016259582$, the simple ratio of universal physical-chemical molar volume constant $[(tg^3\alpha)_K / (2 \cdot 10^3)]^{1/4} \approx V_0 = 0,0224139682$ $m^3 \cdot k \cdot mol^{-1}$.

Found almost simultaneous move two periodicals dependencies molar volume V_E elements and their temperature coefficient $k_t = (T_B + T_M) / (T_B - T_M)$ from the sequence number of the chemical elements. Based on this fact, was made the forecast values of V_E, and calculated on the specific density (d_E) t of the all elements Tran's uranium series items. Experimental determination

Conducted a comparison of the stability of atoms and stars on the example of the analysis of the periodic dependence of the specific density (d_E) all of the 118 known elements today from their serial number. Also was the proposed graduation of four a limited bounders, and eight zones of stability to the same a stars stability of the transitions in similar vision in accordance with the periodic changes in the properties of the respective chemical elements with same mass multiplicity sight for cosmological masses. Namely, for the stars — $M_* = M_E \times M_\odot$ same as for the atomic masses same — $m_E = M_E \times m_u$. In addition, show that limit for atoms and you allow vision grown to the multiplicity of the masses $(308 \div 312)$ of the respective units, i.e. sight $(M_*)_{max} = (308 \div 312) \times M_\odot$, as for atoms — $(m_E)_{max} = (308 \div 312) \times m_u$ corresponding isotope of the elements with sequential numbers from N_E with 118 to 126.

Keywords: melting and boiling point, chemical elements, chemical compounds, molar volume, density, fundamental constants, constant of gravitation, fine structure constant, trans uranium elements, the atom mass limit.

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DIRECT SYNTHESIS AND CRYSTAL STRUCTURE OF BIS(BROMIDO-BIS(1,10-PHENANTHROLINE)-COPPER(II)) NITROPRUSSIDE DIMETHYLFORMAMIDE SOLVATE

The title compound, $[Cu(C_{12}H_8N_2)_2Br]_2[Fe(CN)_5(NO)] \cdot C_3H_7NO$, was prepared by the self-assembly of nitroprusside anion and Cu cation containing a bidentate amine in the reaction of copper powder and sodium nitroprusside with NH_4Br and 1,10-phenanthroline (phen) in dimethylformamide (DMF). The complex is formed of discrete $[Cu(phen)_2Br]^+$ cations, nitroprusside $[Fe(CN)_5(NO)]^{2-}$ anions and DMF molecules of crystallization. The cation has no crystallographically imposed symmetry; the metal atom coordinates two nitrogen atoms of two phen molecules and bromide ion. The copper coordination geometry is intermediate between a square pyramid and a trigonal bipyramid. The $[Fe(CN)_5(NO)]^{2-}$ anion is located on an inversion centre with the nitrosyl group modelled as disordered with one of the CN groups. The DMF solvent molecule was found to be disordered about the crystallographic inversion centre; geometries were restrained to ideal values. In the solid state, alternating layers of cations and of anions plus DMF molecules are stacked along the b axis.

Keywords: crystal structure, intermediate coordination geometry of copper(II), nitroprusside anion, disorder, layers of cations and of anions.

The $[Cu(phen)_2]^{2+}$ cations (phen is 1,10-phenanthroline) whose apical sites can be filled by incoming bridges have been utilized as useful tectons for the construction of heterometallic compounds with desirable properties. Self-assemblies of $[Cu(phen)_2]^{2+}$ and oxovanadium organophosphonates produced remarkable two- and three-dimensional materials [1]. Five different copper (II)-phenanthroline species were found to coexist in the crystal packing of inorganic-metalorganic hybrids based on Keggin polyoxometalates and copper(II)-phenanthroline-oxalate complexes [2]. $[Cu(phen)_2]^{2+}$-$[W^V(CN)_8]^{3-}$ molecular assemblies with the W^V-CN-Cu^{II} linkage showed pronounced ferromagnetic W^V-Cu^{II} coupling for the equatorial cyano bridge at the Cu(II) center [3]. However, the combination of $[Cu(phen)_2]^{2+}$ and pentacyanometalate, for instance, $[Fe(CN)_5(NO)]^{2-}$, was rarely reported.
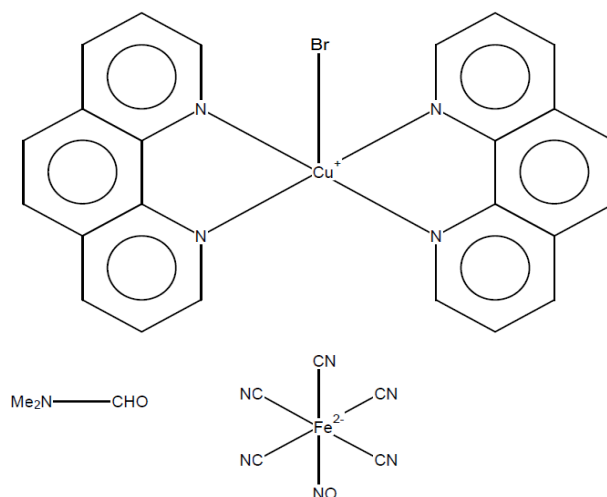
A synthetic strategy developed in our group – direct synthesis of coordination compounds – employs metal

powders or metal oxides as starting materials to obtain novel metal complexes of various nuclearities and structures. Building blocks that are generated *in situ* from zerovalent metals and simple common ligands such as ethylenediamine [4–7], aminoalcohols [8] or Schiff bases [9], subsequently self-assemble with other metal centres present in the same reaction vessel.

Earlier, we have shown that sodium nitroprusside could be used as a source of metalloligand in direct synthesis of heterometallic Cu/Fe complexes [10]. Here, we report on the synthesis and crystal structure of a new cation-anion Cu/Fe complex prepared by the self-assembly of nitroprusside anion and Cu cation containing a bidentate amine. The title compound was isolated from the solution obtained by reacting copper powder and sodium nitroprusside with NH_4Br and 1,10-phenanthroline in dimethylformamide (DMF). To the best of our knowledge the title compound has not been structurally characterized.

The title compound, $[Cu(phen)_2Br]_2[Fe(CN)_5(NO)]\cdot DMF$, is formed of discrete $[Cu(phen)_2Br]^+$ cations, nitroprusside $[Fe(CN)_5(NO)]^{2-}$ anions and DMF molecules of crystallization. The $[Cu(phen)_2Br]^+$ cation has no crystallographically imposed symmetry (Fig. 1). The metal atom is five-coordinate with four nitrogen atoms of two phen molecules and bromide anion. The Cu–N distances vary from 2.007(3) to 2.157(4) Å, the Cu–Br bond is 2.4365(8) Å (Table 1). The *cis* angles at the copper atom are in the range of 80.35(15)–112.00(10)°, the two *trans* angles are equal to 142.06(10) and 172.83(15)°. The angular structural index parameter, $\tau = (\beta-\alpha)/60$, evaluated from the two largest angles ($\alpha < \beta$) in the five-coordinated geometry with the ideal values of 1 for an equilateral bipyramid and 0 for a square pyramid [11], is equal to 0.52. Hence, the copper coordination geometry in the cation is intermediate between a square pyramid and a trigonal bipyramid. A similar coordination geometry was observed in other complexes containing $[Cu(phen)_2Br]^+$ cations [12].
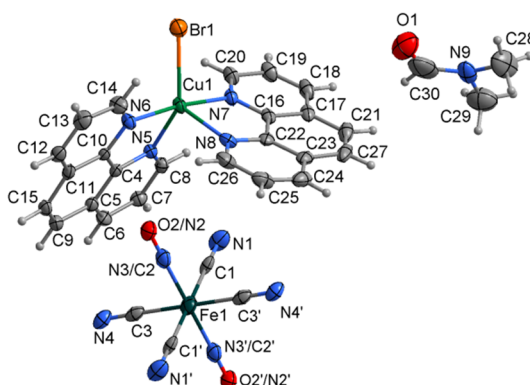

Fig. 1. Molecular structure of $[Cu(phen)_2Br]_2[Fe(CN)_5(NO)]\cdot DMF$ with the numbering scheme. The non-hydrogen atoms ellipsoids are shown at the 50 % probability level

The Fe atom of nitropusside occupies an inversion center, giving rise to a disorder of the nitrosyl group between two trans positions (Fig. 1). The Fe–N/C bond distances in the range 1.846(5)–1.935(5) Å (Table 1) correspond to those typically observed in the $[Fe(CN)_5NO]^{2-}$ anion [13]. The structure is completed by dimethylformamide solvent molecules that were found to be disordered about the crystallographic inversion centre.

In the solid state, layers of $[Cu(phen)_2Br]^+$ cations and of nitroprusside anions plus DMF molecules alternate in the *b* direction. In a layer, the cations are arranged in stacks propagating along the *c* axis with the adjacent stacks lying antiparallel to each other. The neighboring cations in a stack are inverson-related and display π–π stacking between coplanar phen molecules with the ring centroid distances of around 3.6–3.7 Å (Fig. 2). The copper atoms are arranged an a zig-zag fashion with two alternating Cu⋯Cu separations being about 6.94 and 8.77 Å. In a layer, the $[Fe(CN)_5NO]^{2-}$ anions are stacked identically one above the other in the *a* direction alternating with stacks of DMF molecules. The crystal packing does not shows any C–H⋯Br contacts below the van der Waals contact limit. The shortest distance between bromide atoms of above 4.74 Å does not suggest any Br⋯Br interactions either.

Selected bond lengths [Å] and angles [°] for [Cu(phen)₂Br]₂[Fe(CN)₅(NO)]·DMF

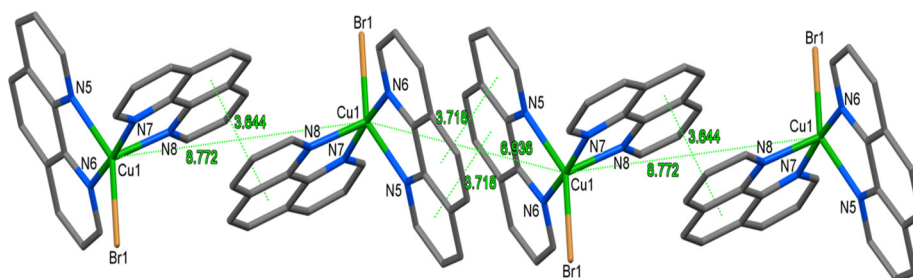|			
Cu(1)-N(6)	2.007(3)	Fe(1)-C(1)	1.846(5)
Cu(1)-N(7)	2.008(4)	Fe(1)-C(3)	1.902(5)
Cu(1)-N(5)	2.080(3)	Fe(1)-N(3)	1.935(5)
Cu(1)-N(8)	2.157(4)		
Cu(1)-Br(1)	2.4365(8)		
N(6)-Cu(1)-N(7)	172.83(15)	C(1)-Fe(1)-C(3)	91.4(2)
N(6)-Cu(1)-N(5)	81.37(14)	C(1)-Fe(1)-N(3)	89.77(19)
N(7)-Cu(1)-N(5)	93.36(14)	C(3)-Fe(1)-N(3)	90.40(19)
N(6)-Cu(1)-N(8)	96.37(15)		
N(7)-Cu(1)-N(8)	80.35(15)		
N(5)-Cu(1)-N(8)	105.92(14)		
N(6)-Cu(1)-Br(1)	95.55(11)		
N(7)-Cu(1)-Br(1)	91.59(11)		
N(5)-Cu(1)-Br(1)	142.06(10)		
N(8)-Cu(1)-Br(1)	112.00(10)		

Fig. 2. π–π Stacking between coplanar phen molecules in a stack of the inverson-related [Cu(phen)₂Br]⁺ cations of [Cu(phen)₂Br]₂[Fe(CN)₅(NO)]·DMF

Crystal data and structure refinement for [Cu(phen)₂Br]₂[Fe(CN)₅(NO)]·DMF

Empirical formula	$C_{56}H_{39}Br_2Cu_2FeN_{15}O_2$
Formula weight	1296.77
Wavelength	0.71073 Å
Crystal system	Triclinic
Space group	$P\bar{1}$
Unit cell dimensions	a = 10.001(3) Å
	b = 10.442(3) Å
	c = 12.598(3) Å
	α = 79.276(4)°
	β = 86.097(4)°
	γ = 81.239(4)°
Volume	1276.5(6) Å³
Z	1
Density (calculated)	1.687 Mg/m³
μ	2.732 mm⁻¹
Crystal size	0.30 x 0.21 x 0.05 mm³
Reflections collected	11025
Independent reflections	5257 [R(int) = 0.035]
Data / restraints / parameters	5257 / 16 / 378
Goodness-of-fit on F^2	1.079
Final R indices [I>2σ(I)]	$R1$ = 0.0501, $wR2$ = 0.1367
R indices (all data)	$R1$ = 0.0743, $wR2$ = 0.1492
Largest diff. peak and hole	0.946 and –1.066 e.Å⁻³

Crystal structures of more than 500 metal complexes including [Cu(phen)₂X]⁺ cations with 1,10-phenanthroline and its derivatives are found in the Cambridge Database [14]. The copper atoms are five- or six-coordinate with similar Cu–N bond lengths to that of the title complex, with only slight deviations. The Database contains about 160 structures of pentacyanonitrosylferrate(II) complexes that comprise both mono- and heterometallic compounds. The nitroprusside anion exists either as anion or coordinates to another metal ion (Na, Mn, Fe, Ni, Cu, Zn, Ag, Sn, Sm, Dy, Hg) through its one, two or four cyano nitrogen atoms, providing di- and polynuclear molecular aggregates as well

as one- and two-dimensional networks. A search for [Cu(phen)₂X]ⁿ⁺–[Fe(CN)₅(NO)]²⁻ metal complexes yielded 4 hits (AFEGUP, HUKWAM, HUKWEQ, QECGAI) with X = Cl⁻, CN⁻ and phen, that were synthesized in our group.

Synthesis of [Cu(phen)₂Br]₂[Fe(CN)₅(NO)]·DMF. Copper powder (0.08 g, 1.25 mmol), NH₄Br (0.24 g, 2.45 mmol), Na₂[Fe(CN)₅(NO)]·2H₂O (0.37 g, 1.25 mmol), phen·H₂O (0.50 g, 2.5 mmol), and 20 ml DMF were heated to 323–333 K and magnetically stirred until total dissolution of the copper was observed (70 min). The resulting green solution was filtered and allowed to stand at room temperature. Dark-green plate-like microcrystals of the title

compound were formed within two days. They were collected by filter-suction, washed with dry Pr^{i}OH and finally dried *in vacuo* (yield: 26 %). IR solid v(cm^{-1}): 2150m, 1900vs, 1690m, 1600s, 1520w, 1430s, 1380m, 1230w, 1150w, 1110w, 1000w, 860vs, 790w, 720vs, 680vw.

Experimental. Crystallographic data for the structure were collected at 150(2) K on a Bruker SMART diffractometer fitted with Mo Kα radiation. Following multi-scan absorption corrections and solution by direct methods, the structure was refined against F^2 with full-matrix least-squares using the program [15]. The DMF solvent molecule was found to be disordered about a crystallographic inversion centre the geometries of which were restrained to ideal values. All hydrogen atoms were added at calculated positions and refined by use of a riding model with isotropic displacement parameters based on those of the parent atoms. Anisotropic displacement parameters were employed throughout for the non-hydrogen atoms. The crystal data for [Cu(phen)$_2$Br]$_2$[Fe(CN)$_5$(NO)]·DMF are summarized in Table 2.

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ПРЯМИЙ СИНТЕЗ ТА КРИСТАЛІЧНА БУДОВА ДИМЕТИЛФОРМАМІДНОГО СОЛЬВАТУ БІС(БРОМІДО-БІС(1,10-ФЕНАНТРОЛІНО)-КУПРУМУ(II)) НІТРОПРУСИДУ

Катіони [Cu(phen)$_2$]$^{2+}$ (phen – 1,10-фенантролін) були використані як корисні тектони для побудови гетерометалічних сполук з бажаними властивостями. Відомі комплекси, що містять катіон [Cu(phen)$_2$X]$^{n+}$ та нітропрусид-аніон [Fe(CN)$_5$(NO)]$^{2-}$, обмежуються 4-ма сполуками з X = Cl$^-$ та CN$^-$, які було синтезовано нашою групою раніше. Новий комплекс [Cu(phen)$_2$Br]$_2$[Fe(CN)$_5$(NO)]·C$_3$H$_7$NO було одержано в результаті самозбірки за участю нітропрусид-аніона та катіона купруму, що містить бідентатний амін, при взаємодії мідного порошку, нітропрусида натрію, NH$_4$Br і 1,10-фенантроліна в диметилформаміді (ДМФА). Сполука утворена з окремих катіонів [Cu(phen)$_2$Br]$^+$, нітропрусид-аніонів [Fe(CN)$_5$(NO)]$^{2-}$ та сольватних молекул ДМФА. Катіон не має кристалографічної симетрії, атом металу координує чотири атоми нітрогену двох молекул фенантроліну та бромід-іон. Атом купруму демонструє координаційну геометрію, яка є проміжною між тригонально-біпірамідальною та квадратно-пірамідальною. У нітропрусид-аніоні, розташованому в центрі інверсії, нітрозильна група розупорядкована також із однією з груп CN. Молекула розчинника також розупорядкована навколо центра кристалографічної інверсії; її геометрія змодельована з використанням ідеальних параметрів. У кристалі сполуки шари катіонів та такі, що містять аніони і молекули ДМФА, чергуються вздовж осі b. У шарі катіони утворюють колонки, які поширюються вздовж осі b. Сусідні колонки антипаралельні. Катіони в колонці пов'язані π–π стекінгом між копланарними молекулами фенантроліну з відстанями між центроїдами 3,6–3,7 Å. Атоми міді розташовано зигзагоподібно з відстанями Cu···Cu близько 6,94 і 8,77 Å, що чергуються.

Ключові слова: кристалічна будова, проміжна координаційна геометрія купруму(II), нітропрусид-аніон, розупорядкованність, шари катіонів та аніонів.

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ПРЯМОЙ СИНТЕЗ И КРИСТАЛЛИЧЕСКОЕ СТРОЕНИЕ ДИМЕТИЛФОРМАМИДНОГО СОЛЬВАТА БИС(БРОМИДО-БИС(1,10-ФЕНАНТРОЛИНО)-МЕДИ(II)) НИТРОПРУССИДА

Комплекс [Cu(C$_{12}$H$_8$N$_2$)$_2$Br]$_2$[Fe(CN)$_5$(NO)]·C$_3$H$_7$NO был получен в результате самосборки с участием нитропруссид-аниона и катиона меди, содержащего бидентатный амин, при взаимодействии медного порошка, нитропруссида натрия, NH$_4$Br и 1,10-фенантролина (phen) в диметилформамиде (ДМФА). Соединение состоит из отдельных катионов [Cu(phen)$_2$Br]$^+$, нитропруссид-анионов [Fe(CN)$_5$(NO)]$^{2-}$ и сольватных молекул ДМФА. Катион не имеет кристаллографической симметрии, атом металла координирует четыре атома азота двух молекул фенантролина и бромид-ион. Координационная геометрия меди является промежуточной между тригонально-бипирамидальной и квадратно-пирамидальной. В нитропруссид-анионе, находящемся в центре инверсии, нитрозильная группа разупорядочена с одной из групп CN. Молекула растворителя также является разупорядоченной относительно центра кристаллографической инверсии; ее геометрия была приведена к идеальным параметрам. В кристалле комплекса слои катионов и анионов плюс молекулы ДМФА чередуются вдоль оси b.

Ключевые слова: кристаллическое строение, промежуточная координационная геометрия меди(II), нитропруссид-анион, разупорядоченность, катионные и анионные слои.