STACKING INTERACTIONS IN THE CRYSTAL STRUCTURES OF MIXED LIGAND SQUARE-PYRAMIDAL COPPER(II) COMPLEXES WITH AROMATIC 1,10-PHENANTHROLINE OR 2,2′-BIPYRIDINE LIGANDS AND ACETYLACETONATE

Elena Melnic

Institute of Applied Physics, Academy of Sciences of Moldova,
5 Academia str. MD-2028, Chisinau, Republic of Moldova

E-mail: melnic@phys.asm.md

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Abstract

Four novel mononuclear square-pyramidal complexes with composition $[Cu(acac)(phen)(DMF)]BF_4$ (**1**), $[Cu(acac)(phen)(H_2O)]BF_4$ (**2**), $[Cu(acac)(phen)(NO_3)]MeOH$ (**3**) and [Cu(acac)(phen)Cl]MeOH (**4**), (phen = phenanthroline and acac = acetylacetonate) have been synthesized and characterized by single-crystal X-ray diffraction. The supramolecular structures of these novel complexes and related complexes found in the Cambridge Structural Database (CSD), which contain a planar [Cu(acac)(AA)] fragment, where AA denotes phen or 2,2′-bipyridine (bipy)/4,4′-dimethyl-2,2′-dipyridine (Me_2bipy), have been analyzed from in terms of stacking interactions in these systems.

1. Introduction

Noncovalent interactions of aromatic and other π-systems referred to as "π–π stacking" or "stacking interactions" and generally observed in the crystal structures are recognized as specific parallel or about parallel mutual arrangements of interacting fragments. These interactions take place in different settings; they affect the intercalation into DNA, host–guest complexations, and interactions in proteins [1]. These interactions play an important role in crystal packing [2−5], self-assembly processes [6], recognition of aromatic compounds [7−9], and regulation of selectivity in organic reactions [10]; they are significant in biological systems [11]. In the field of crystal engineering, the importance of these weak interactions for the design and control of molecular organization in the solid state has been well recognized; however, the predictability of their existence and settings in the final assembly is still challenging.

These interactions are dominated by dispersion forces with significant contributions of electrostatics and hydrogen bonding [12, 13]. Stacking interactions of organic aromatic molecules have been extensively investigated [14–17]. The most stable stacking interaction for a benzene dimer is a parallel-displaced geometry at an interaction energy of –2.73 kcal/mol [18]. In the context of understanding the fundamentals of stacking interactions, benzene and substituted benzene dimers have been studied to determine the effects of electrostatics, dispersion and charge transfer on stacking stabilization. The energies of stacking interactions of benzene with a chelate ring have been calculated [14]; the results show that chelate–benzene stacking interactions are

remarkably stronger than benzene–benzene interactions. In the arrangement of aromatic rings one can distinguish generally between a stacked arrangement, and an edge- or point-to-face, T-shaped conformation [19]. Stacking does not necessarily assume only a perfect face-to-face alignment of π-systems; more often, it can be an offset or slipped packing.

The involvement of planar chelate rings (metallacycles) of transition metals complexes in the stacking interactions have been recently recognized and described [20]. It has been shown that the geometries of stacking interactions between chelate rings [21] or between chelate rings and aromatic rings [22] are similar to stacking interactions between the aromatic rings.

Rational design of metal-organic materials with required architecture and properties is in focus of crystal engineers and materials scientists. In terms of crystal engineering, π–π stacking interactions are relatively weak and also only weakly directional. They are therefore difficult to predict and control, especially in the presence of other stronger interactions, such as strongly directional coordination and hydrogen bonds.

The ability of first-row transition metals to form complexes with ligands, such as 1,10-phenanthroline (phen), 2,2'-bipyridine (bipy) or acetylacetonate (acac), is well known. Interest in copper complexes of phen and 2,2'-bipy is stemming from their potential application as antimicrobial, antiviral, anti-inflammatory, antitumor agents, enzyme inhibitors, or chemical nucleases. From crystal engineering perspective, the square-pyramidal Cu(II) complexes with chelating aromatic ligands are attractive candidates to design extended supramolecular architectures by π–π interactions involving metallacycles [23–25].

The aromatic chelate ligands attached to copper(II) (bipy, phen and related molecules) favor the intermolecular π–π stacking interactions involving metallacycle; these interactions play an important role in sustaining extended supramolecular solid-state architectures [26]. The phen molecule coordinating to a metal ion forms a large planar system of four fused rings: two pyridine fragments, one C_6-ring and one chelate ring [27] and the smaller bipy ligand, which comprises three rings with the metal ion (two pyridine and one chelate rings) and exhibiting an increasing tendency to form stacking interactions with the π-systems of various aromatic groups [28]. The tendency for stacking interactions to occur is an important issue when using phenanthroline complexes in various fields; it facilitates the prediction of crystal structure architecture [29–31]. The preservation of robust π–π stacking motifs in crystal and even in solution has been widely explored and summarized in a number of research and review articles [19, 32–39].

For the systematical study of the geometry of the stacking interactions with participation of a chelate ring in the structures of square-pyramidal Cu(II) complexes, four novel neutral and cationic complexes containing a [Cu(acac)(phen)] fragment have been synthesized and structurally characterized by single-crystal X-ray diffraction. The statistical analysis of the geometry of stacking interaction in these novel compounds and all available literature data including the related complexes with [Cu(acac)(bipy)] and [Cu(acac)(Me_2bipy)] fragments has been carried out.

2. Results and discussion

Four novel mononuclear complexes with compositions [Cu(acac)(phen)(dmf)]BF_4 (**1**), [Cu(acac)(phen)(H_2O)]BF_4 (**2**), [Cu(acac)(phen)(NO_3)]MeOH (**3**) and [Cu(acac)(phen)Cl]MeOH (**4**) were synthesized by interaction of $Cu(BF_4)_2 \cdot H_2O$ (for **1** and **2**), $Cu(NO_3)_2 \cdot 2H_2O$ (for **3**) and $CuCl_2 \cdot 3H_2O$ (for **4**) with phen and acac. Components were dissolved in a MeOH/DMF mixture for **1** and **4** and a MeOH/THF mixture for **3** and in MeOH for **2,** MeOH = methanol;

DMF = demethylformamide; THF = tetrahydrofuran.

The crystal structures of all compounds were investigated by single-crystal X-ray diffraction. Diffraction data for **1**−**4** were recorded at room temperature on an Oxford Diffraction Xcalibur diffractometer equipped with a CCD area detector and a graphite monochromator utilizing MoK_α radiation. Final unit cell dimensions were obtained and refined on an entire data set. Structures were solved by direct methods using the SHELX-97 program package [40] and refined with the full-matrix least-squares method with anisotropic thermal parameters for the non-hydrogen atoms. All compounds crystallize in the triclinic system, space group *P*-1. In all structures, the C(sp^2)-bound H atoms were placed in calculated positions and treated using a riding model approximation with $U_{iso}(H) = 1.2U_{eq}(C)$; H atoms of the methyl groups were found and refined using AFIX 137 instruction and $U_{iso}(H) = 1.5U_{eq}(C)$, while the O-bound hydrogen atoms were found from differential Fourier maps at intermediate stages and their positions were refined using restrains. Figures were produced by Mercury [41]. X-ray data and details of the refinement for **1**−**4** are summarized in Table 1.

Crystallographic data in CIF format for **1**−**4** reported herein were deposited with the Cambridge Crystallographic Data Centre and allocated the deposition numbers **CCDC 1520778-1520781**. These data can be obtained free of charge from the Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

Table 1. Crystal and structure refinement data for **1**–**4**

Compound	**1**	**2**	**3**	**4**
Empirical formula	$C_{20}H_{22}N_3O_3B_1F_4Cu$	$C_{17}H_{17}N_2O_3B_1F_4Cu$	$C_{17.5}H_{17}N_3O_{5.5}Cu$	$C_{18}H_{19}N_2O_3Cl_1Cu$
Formula weight	502.75	447.67	420.88	410.34
T (K)	293(2)	293(2)	293(2)	293(2)
Crystal system	Triclinic	Triclinic	Triclinic	Triclinic
Space group	*P*-1	*P*-1	*P*-1	*P*-1
Z	2	2	2	2
a, Å	9.8080(7)	8.3319(7)	8.6096(9)	8.9974(7)
b, Å	11.2159(8)	11.0211(10)	10.2314(7)	9.2215(7)
c, Å	12.0344(8)	12.1245(13)	12.1027(13)	12.0605(10)
α, (º)	62.796(7)	65.264(9)	105.200(7)	102.498(7)
β, (º)	73.679(6)	78.974(8)	104.230(9)	97.666(7)
γ, (º)	72.459(6)	68.614(8)	108.009(7)	106.561(7)
V, $Å^3$	1106.5(2)	940.6(2)	914.2(2)	915.84(13)
D_{calc} (g cm^{-3})	1.509	1.581	1.529	1.488
μ(mm^{-1})	1.047	1.220	1.231	1.357
F(000)	514	454	432	422
Reflections collected/unique	7405/4921	6325/ 4184	5021/3211	5356/3386
Reflections with $I > 2\sigma(I)$	3044	2660	2193	2357
Data/restraints/parameters	4921 / 0 / 293	4184 / 3 / 261	3211 / 13 / 257	3386 / 0 / 231
GOF on F^2	1.000	0.999	0.999	1.001
R_1, wR_2 [$I > 2\sigma(I)$]	0.0681, 0.1322	0.0631, 0.1415	0.0617, 0.1419	0.0548, 0.0996
R_1, wR_2 (all data)	0.1140, 0.1700	0.1097, 0.1805	0.0975, 0.1628	0.0892, 0.1157
$\Delta\rho_{max}$, $\Delta\rho_{min}$, (e·$Å^{-3}$)	0.696, -0.503	0.397, -0.316	0.744, -0.347	0.369, -0.442

The structures of all compounds reveal square pyramidal 4+1 copper (II) N_2O_3 environment in **1**, **2**, **4** and N_2O_2Cl in **3**, where the equatorial planes are fixed by the chelate acac and phen ligands, which form six- and five-membered metallacycles, respectively (Fig. 1). Axial position is occupied by oxygen atom of DMF in **1**, H_2O in **2**, NO_3 in **3** and chlorine atom in **4**. Complexes **1** and **2** are cationic and comprise BF_4^- counteranions in the structure, while complexes **3** and **4** are neutral methanol solvates. In **1**, **2** and **3** the distances in equatorial plane are in the range Cu–O 1.890–1.919 Å, Cu–N 2.004–2.015 Å, and $Cu–O_{(axial)}$= 2.340–2.366 Å, while in **4** these distances are Cu–O 1.919–1.923 Å, Cu–N 2.016–2.031 Å, and $Cu–Cl_{(axial)}$ = 2.529 Å. In crystal **1** two mononuclear units related by a center of symmetry exhibit extended π–π stacking interactions involving both metallacycles and chelate phen ligands, which overlap in a face-to-face manner with an interplanar separation 3.316 Å and centroid···centroid distances of 3.783, 3.629, and 3.601 Å for acac metallacycle···phenyl moiety of phen, acac metallacycle···pyridine moiety of phen and phen metallacycle···phen metallacycle pairs, respectively (Fig. 1a). The distance between the copper atoms within the supramolecular dimers is 5.267 Å.

The molecular packing in crystal structure **2** reveals the intermolecular π–π stacking interactions between the center symmetry related complexes with interplanar separation of 3.390 Å and the distance between centroids of phen metallacycle and pyridine moiety of the phen ligand of 3.580 Å. The acac is not involved in stacking and dimer formation. These dimers are further stacked with the neighbor one by another side of the phen ligand with the shortest distance between centroids of the overlapped ring of 3.469 Å and interplanar spacing of 3.285 Å (Fig. 1b). These interactions result in a well-defined and easily recognized extended 1-D supramolecular motif along the crystallographic *c* axis.

In neutral complexes **3** and **4** the centre symmetric dimer is formed due to stacking interaction of exclusively acac metallacycles which lie in parallel planes with separations of 3.478 and 3.637 Å and centroid···centroid distances of 3.444 Å and 3.591 Å, respectively. As in the case of **1** and **2**, these dimers further interact through staking interactions involving phen ligands by overlaping of the phenyl and pyridine moieties. Interplanar phen···phen separations of 3.176 and 3.331 Å, distances between centroids within the dimer are 3.697 and 3.797 Å, for **3,** and **4**, respectively (Figs. 1c, 1d). The crystal structures of **3** and **4** revealed again the infinite supramolecular motifs along the [011] crystallographic direction.

The structures of studied complexes revealed that the [Cu(acac)(phen)] fragment is involved in stacking interactions involving metallacycles; these interaction represents the reliable supramolecular synthon suitable to generate a robust supramolecular motif. To investigate the reliability of this supramolecular synthon, all the available reported structures containing the planar [Cu(acac)(phen)] fragment and related [Cu(acac)(bipy)] or [Cu(acac)(Me_2bipy)] were analyzed in terms of stacking interactions in these systems using Cambridge Structural Database (CSD) (version 5.37, 2016).

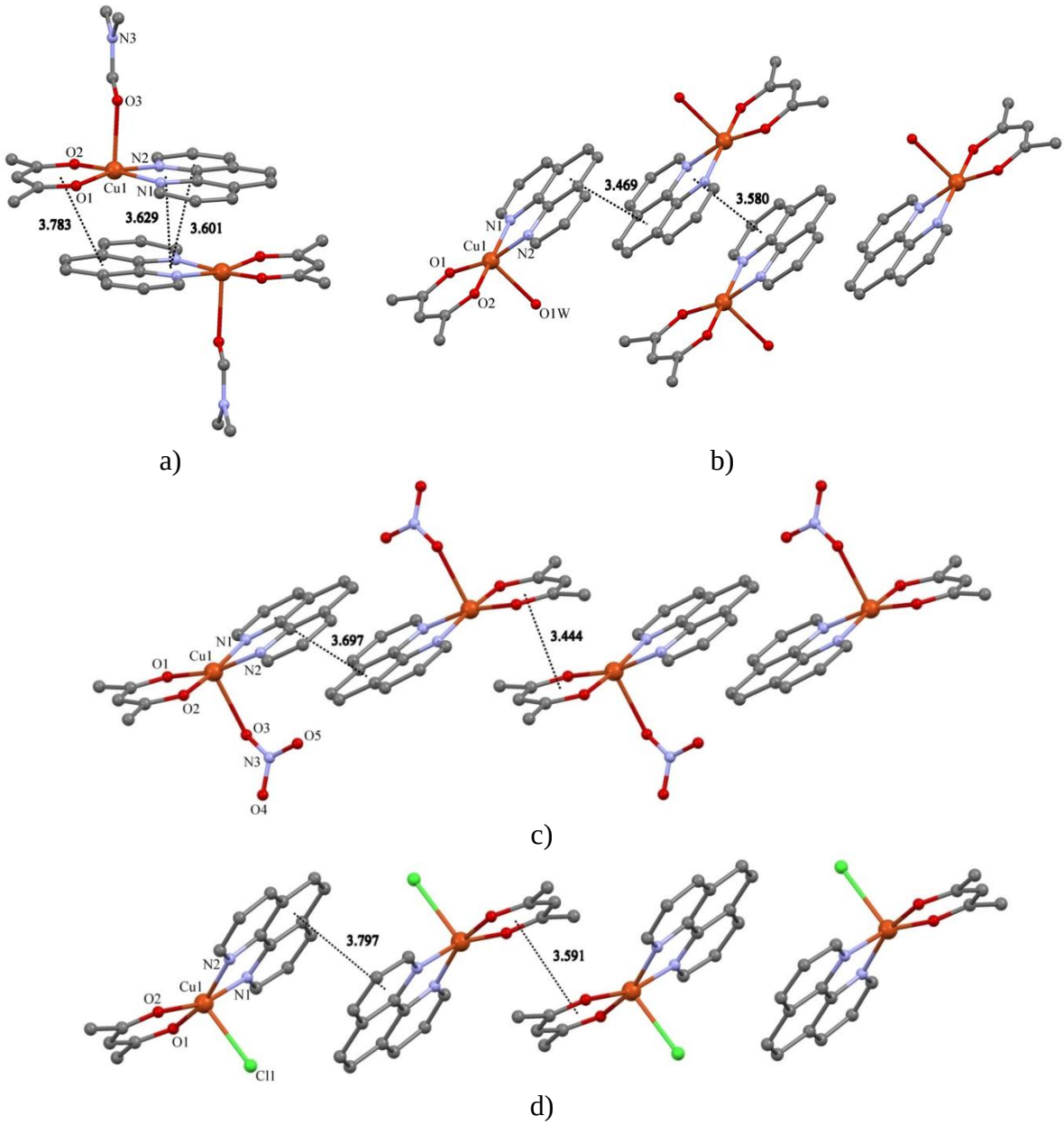


Fig. 1. Stacking interactions in cationic (a) [Cu(acac)(phen)(DMF)]BF_4 (**1**), (b) [Cu(acac)(phen)(H_2O)]BF_4 (**2**) and neutral (c) [Cu(acac)(phen)(NO_3)]MeOH (**3**), and (d) [Cu(acac)(phen)Cl]MeOH (**4**) complexes.

3. Searching methods

The quest in CSD revealed 29 original hits for the [Cu(acac)(phen)] fragment, 19 original hits for the [Cu(acac)(bipy)] fragment, and 5 original hits for the [Cu(acac)(Me_2bipy)] fragment. The structures for which atomic coordinates were not available or structures containing non-pyramidal complexes, or co-crystals containing another planar complex (in total 7 hits) were excluded from further consideration. Thus, 49 structures including four reported above

complexes were analyzed. To find intermolecular stacking interactions between [Cu(acac)(AA)] fragments, where AA denotes phen or 2,2′-bipyridine (bipy)/4,4′-dimethyl-2,2′-dipyridine (Me_2bipy) aromatic molecule, at least one of three searching criterions should be satisfied: the first criterion assumes that the distance between centroids of ligand aromatic rings of the neighboring [Cu(acac)(AA)] is below 4.6 Å [19]; the second criteria assumes that the distance between centers of aromatic ring and chelate ring (metallacycles) is shorter than 4.3 Å; and the third criterion is that the distance between centroids of the chelate rings (metallacycles) is below 4.2 Å. (Tables 2, 3). Only one from 49 analyzed structures did not reveal stacking interactions, while 98% of the analyzed structures revealed stacking interactions.

4. Stacking interactions of [Cu(acac)(phen)] fragments

The phenanthroline molecule coordinating to a copper ion forms a large planar system of four fused rings: two pyridine rings, one C_6-ring (*phenyl ring*) and one chelate ring. Using the above mentioned criteria, 30 structures with 123 interactions between complexes were found including the four novel structures reported above. In all structures, two complexes are oriented in "head-to–tail" manner (Fig. 2); however, they show many different overlap geometries resulting in different Cu···Cu intermolecular distances within the dimer formed by stacking interactions.

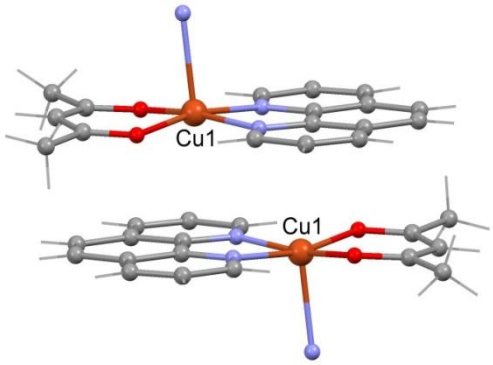
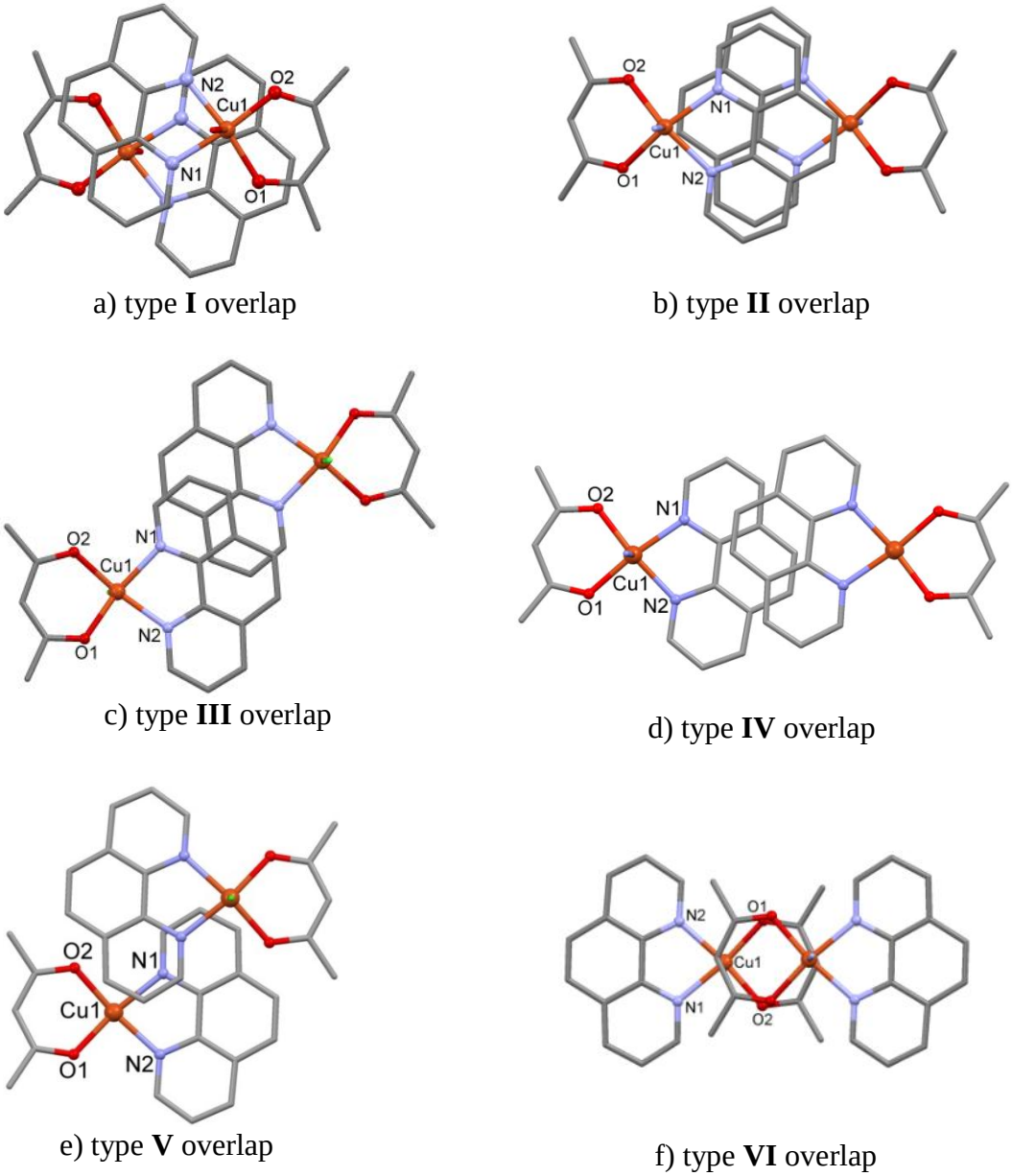


Fig. 2. Head-to-tail orientation of the [Cu(acac)(phen)] fragments.

Based on the preliminary analysis of possible interacting geometries, six types of mutual arrangement of fragments in the stacking were identified (Fig. 3). The group of structures with overlap type I is the most numerous and includes 17 structures and 85 interactions (Table 2).

The intermolecular distances between the centroids of any ring in the dimer: $d_{Py\text{-}Py}$, $d_{Ph\text{-}Py}$, $d_{Py\text{-}M}$, $d_{ac\text{-}Py}$, $d_{Ph\text{-}Ph}$, $d_{Ph\text{-}M}$, $d_{Ph\text{-}ac}$, $d_{ac\text{-}M}$, and $d_{\ ac\text{-}ac}$ were measured. Distances $d_{Py\text{-}Py}$, $d_{Ph\text{-}Py}$, $d_{Py\text{-}M}$, and $d_{ac\text{-}Py}$ are the intermolecular separations between the centroids of two pyridine fragments, one pyridine fragment and C_6-ring, one pyridine fragment, two chelate rings and two C_6-rings, respectively. The values $d_{Ph\text{-}M}$ and $d_{Ph\text{-}ac}$ are distances between the centroids of C_6 and chelate rings (metallacycle); however, $d_{ac\text{-}M}$ and $d_{ac\text{-}ac}$ are the distances between two chelate rings (metallacycles), respectively (Table 2). In the structures with relatively short Cu···Cu distance (3.562–5.604 Å) in the stacking, an overlap takes place according to types **I** (17 hits) and **VI** (4 hits)**.** Type **I** shows the most extended overlap area and includes both metallacycles and phen rings (Figs. 3a, 3f) [23, 25, 42–45], and for type **VI** the only acac metallacycles are overlapped [46, 47] and result in the shortest centroid···centroid distances of 3.200–3.591 Å. The overlap

according to type **II** with the Cu···Cu distance in a range of 5.732–6.713 Å was found in **6** structures and involves phen metallacycles and penyl C_6 moiety, as well as pyridine···pyridine moiety of phen ligands, in stacking (Fig. 2b). Overlap types **III** (7 hits) and **IV** (7 hits) are somewhat similar; only the rings of phen ligands participate in the overlap: phenyl···pyridine and pyridine···pyridine overlap takes place in **III**, and phenyl···phenyl and phenyl···pyridine in **IV** (Figs. 3c, 3d) [44, 46–51]. The Cu···Cu distances are in a range of 8.344–9.270 Å. Metallacycles are not involved in the overlapping for type **III** and **IV**. Only two hits were found for type **V** overlap with a small overlapping area (Fig. 2e) and Cu···Cu distances of 6.591 and 6.627 Å [48, 49]. Only in one crystal structure (Ref.code KEBYOG) [46] no π–π stacking interaction was found between the complexes. A histogram of hit distribution over the different types of [Cu(acac)(phen)] overlap in the stacking is shown in Fig. 4.



a) type **I** overlap

b) type **II** overlap

c) type **III** overlap

d) type **IV** overlap

e) type **V** overlap

f) type **VI** overlap

Fig. 3. The different types of [Cu(acac)(phen)] fragment overlap in stacking; view perpendicular to the plane of the overlapping fragments.

Table 2. Parameters of stacking interactions in the structures of complexes with the [Cu(acac)(phen)] fragment

Composition, Space group	overl ap type	Centroid–centroid distances (Å)										*P-to-P* distance or angle (Å/°)*	Cu—Cu distance (Å)	Reference, refcode in CSD
		$d_{Py\text{-}Py}$	$d_{Ph\text{-}Py}$	$d_{Ph\text{-}Ph}$	$d_{Py\text{-}M}$	$d_{Ph\text{-}M}$	$d_{ac\text{-}Ph}$	$d_{ac\text{-}Py}$	$d_{ac\text{-}M}$	$d_{ac\text{-}ac}$	$d_{M\text{-}M}$			
[Cu(acac)(hfac)(phen)], *P*-1	I, IV	3.820	3.983	3.475	3.884	3.967	3.671	—	—	—	3.465	3.361/3.417	5.178/8.677	[44] ACFCUA
[Cu(acac)(phen)(OH_2)][hfac]·H_2O, *P*-1	I, III	3.970/ 3.594	3.994	—	3.675	4.151	3.760	—	—	—	3.698	3.352/3.344	5.324/8.344	[44] ACFCUB
[Cu(acac)(phen)(H_2O)]ClO_4, *P*-1	I, IV	—	3.951	3.729	—	—	—	3.709	3.594	—	—	3.350/3.439	3.744/9.168	[44] ACIFIC
[{Cu(acac)(phen)}$_2${Ni(CN)$_4$}]·H_2O, *P*-1	I, IV	3.978	3.735	4.025	3.646	4.151	3.827	—	—	—	3.865	3.329/3.372	5.604/9.153	[25] DOZSER
[{Cu-(acac)(phen)}$_2$(μ-bpp)](ClO_4)$_2$·$6H_2O$, $P4_2/n$	I, IV	—	3.950	3.639	3.944	—	3.973	3.646	—	—	4.160	3.350/3.428	4.810/8.990	[24] FAZZIQ
[Cu(acac)(phen)Cl], *P*-1	III, V	3.843/ 3.744	3.763	—	3.923	—	—	—	—	—	—	3.443/3.234	8.520/6.591	[48] FOWJEH
[Cu(acac)(phen)(NCS)], *P*-1	II	3.523	3.937	4.235	3.983	3.561	—	—	—	—	—	3.480	6.668	[23] JAJSOD
[{Cu(acac)(phen)(NCS)}$_2${($ClHg)_2$(NCS)$_2$}], *P*-1	I	—	—	—	—	—	3.752	3.469	3.809		4.058	3.347	3.825	[23] JAJTAQ
[{Cu(acac)(phen)(NCS)}$_2$ $Hg(SCN)_2$], *C*2/*c*	II	3.710	3.740	4.203	—	3.625	—	—	—	—	—	3.522	6.713	[23] JAJTEU
[{Cu(acac)(phen)}$_2$ ($\mu_{1,1}$-N_3)](ClO_4)}·$2H_2O$, *P*-1	IV,VI	—	3.653	4.080	—	—	—	—	—	3.430	—	3.193/3.459	8.956/5.167	[46] KEBYIA
[Cu(acac)(phen)(H_2O)]NO_3} (NO_3)·H_2O, *P*-1	II	3.549	4.046	4.406	3.884	3.530	—	—	—	—	—	3.484	6.203	[52] KUZWAD
[Cu(acac)(phen)Br], *P*-1	III, V	3.986/ 3.754	3.900	—	3.928	—	—	—	—	—	—	3.533/3.297	8.745/6.627	[49] LIVNOU
[Cu(acac)(phen)]BPh_4, *P*-1	I	—	—	—	—	—	3.593	3.859	3.582	—	—	3.437	3.562	[42] NEKBUC
[Cu(acac)(phen)(dmso)]BPh_4, *P*-1	I	—	—	—	3.671	—	3.644	4.046	—	—	—	3.279	4.902	[42] NEKCEN
[Cu(acac)(phen)(dmf)]BPh_4, $P2_1/c$	I	—	—	—	—	—	3.688	3.589	3.659	—	—	3.377	3.815	[42] NEKCIR
[Cu(acac)(phen)(acetone)]BPh_4, *P*-1	I	—	—	—	3.683	—	3.636	4.004	—	—	—	3.273	4.853	[42] NEKCOX
[Cu(acac)(phen)(CH_3CN)] (CH_3CN) BPh_4, *P*-1	II	3.797	3.867	—	3.403	3.927	—	—	—	—	—	3.256	6.153	[42] NEKCUD
[Cu(acac)(phen)](CH_3NO_2) BPh_4, *P*-1	II	3.678	4.052	—	3.477	3.748	4.181	—	—	—	—	3.308	5.732	[42] NEKDAK
[Cu(acac)(phen)(py)]BPh_4, *P*-1	I	—	—	—	—	—	3.631	3.568	3.941	—	—	3.370	4.134	[42] NEKFAM
[Cu(acac)(phen)(hmpa)]BPh_4, *C*2/*c*	II	3.782	3.767	—	3.518	3.782	—	—	—	—	—	3.389	6.365	[42] NEKFEQ
[Cu(acac)(phen)(NO_3)]·H_2O, *C*2/*c*	I, III	3.745	3.668	—	3.942	3.842	3.754	—	—	—	3.585	3.375/3.364	5.463/8.886	[50] OCOKOG
[Cu(acac)(phen)$_2$Ag(CN)$_2$](ClO_4), *P*-1	I	3.700	—	—	3.792	3.914	3.736	—	—	—	—	3.385	5.372	[43] RELSEH
[Cu(acac)(phen)$_2$Au(CN)$_2$](ClO_4), *P*-1	I	3.644	—	—	3.854	—	3.656	3.757	—	—	—	0.54	4.695	[43] RELSIL
[{Cu(acac)(phen)}$_2${Au(CN)$_2$}] (ClO_4)·0.5CH_3CN, *P*-1	I	—	3.974	—	—	—	—	3.690	3.596	—	—	3.323/0.64	3.693/8.47	[43] RELSOR
[Cu(acac)(phen)(C_2N_3)]·H_2O, *P*-1	III, VI	—	3.781	4.245	—	—	—	—	—	3.200	—	3.418/3.255	9.270/5.011	[47] SUXRUZ
[Cu(acac)(phen)(ClO_4)][Cu(acac) (phen)(CH_3CN)]ClO_4, $P2_1/c$	III	4.082	3.837	—	—	—	—	—	—	—	—	3.657	8.437	[51] YOTXOU
[Cu(acac)(phen)(DMF)]BF_4, *P*-1	I	3.905	—	—	3.601	4.086	3.783	—	—	—	3.629	3.316	5.267	Compound **1**
[Cu(acac)(phen)(H_2O)]BF_4, *P*-1	I, IV	3.938	—	3.460	3.580	4.060	4.043	—	—	—	3.790	3.390/3.285	5.609/9.252	Compound **2**
[Cu(acac)(phen)(NO_3)]MeOH, *P*-1	IV, VI	—	3.697	4.025	—	—	—	—	—	3.444	—	3.176/3.478	9.095/5.190	Compound **3**
[Cu(acac)(phen)Cl]MeOH, *P*-1	III, VI	3.812	3.797	—	—	—	—	—	—	3.591	—	3.331/3.637	8.620/5.641	Compound **4**

* interplanar distance or dihedral angle between about parallel planes.

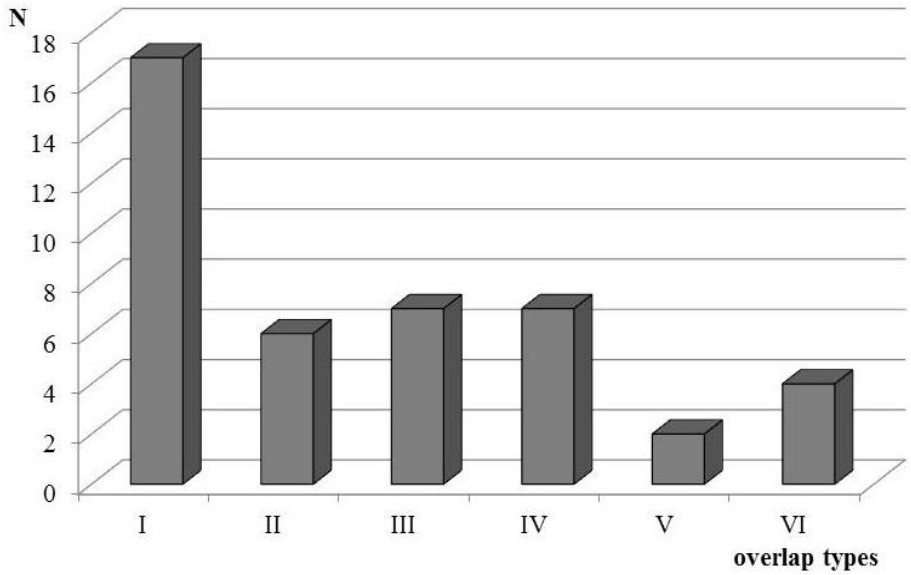


Fig. 4. Histogram of hit distribution over the different types of [Cu(acac)(phen)] overlap in the stacking

Histogram 4 and Table 2 show that metallacycles are involved in stacking interactions in 29 from 30 analyzed structures (96.7%) (overlap types **I**, **II**, **V,** and **VI**).

5. Stacking interactions of [Cu(acac)(bipy)] or [Cu(acac)(Me$_2$bipy)] fragments

A similar analysis was conducted for the related complexes containing planar [Cu(acac)(bipy)] or [Cu(acac)(Me$_2$bipy)] fragments with less extended aromatic systems. The quest in CSD revealed 18 crystal structures of square-pyramidal complexes: 15 with [Cu(acac)(bipy)] and 3 with [Cu(acac)(Me$_2$bipy)] fragments. Analysis of search results showed that bipy/Me$_2$bipy copper(II) complexes can have two different orientations, namely, head-to-tail and "head-to-head" (Fig. 5).

Based on the analysis of possible interacting geometries of [Cu(acac)(bipy)] or [Cu(acac)(Me$_2$bipy)] fragments, six types of mutual arrangement of fragments in the stacking were identified (Fig. 6). Fourteen structures have a head-to-tail orientation and overlap in four modes (Figs. 6a, 6b, 6e, 6f); four structures are oriented head-to-head (Figs. 6c, 6d) [23, 25, 42, 43, 49, 53]. The intermolecular distances between the centroids of any ring in the dimmer—$d_{Py\text{-}Py}$, $d_{Py\text{-}M}$, $d_{ac\text{-}py}$, $d_{ac\text{-}ac}$, $d_{ac\text{-}M}$, $d_{M\text{-}M}$—were analyzed. Distances $d_{Py\text{-}Py}$,$d_{Py\text{-}M}$ and $d_{ac\text{-}Py}$ are the intermolecular separations between the centroids of two pyridine fragments, one pyridine fragment and chelate ring, respectively. Separations $d_{ac\text{-}ac,}$ $d_{ac\text{-}M,}$ and $d_{M\text{-}M}$ are distances between the centroids of two chelate rings, respectively (Table 3). The group of structures with the overlap of type **I**, which is similar to that found for the [Cu(acac)(phen)] fragment (Fig. 2a), is the most numerous and includes 9 structures and 24 interactions (Table 3). In the structures with a relatively short Cu···Cu distance (3.570–5.475 Å) in the stacking, the overlap takes place according to types **I** (9 hits), **III** (3 hits), **IV** (1 hit), and **VI** (3 hits). Type **I** shows the most extended overlap area and includes both metallacycles and bipy/Me$_2$bipy rings (Figs. 6a, 6f) [23, 25,42, 43, 46]; for type **VI,** only acac metallacycles overlap [46, 53, 55] and result in the shortest centroid···centroid distances of 3.310–3.495 Å. The overlap in accordance with type **II** with the

Cu···Cu distance in a range of 7.410–7.820 Å was found in five structures and involves only the pyridine···pyridine moiety of bipy/Me_2bipy ligands in stacking (Fig. 6b) [23, 25, 43, 53].

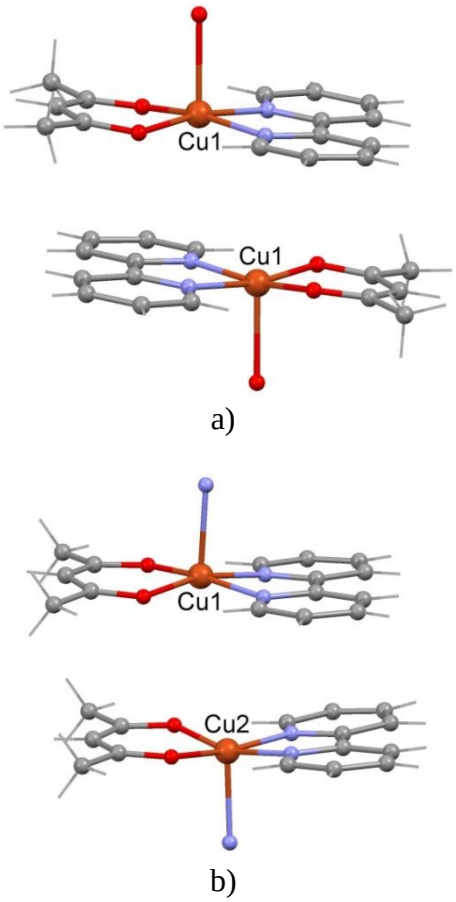
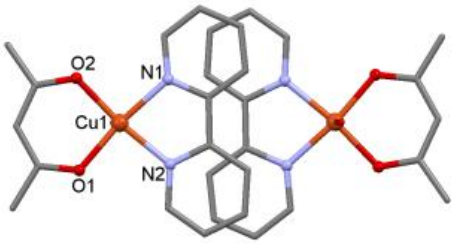


Fig. 5. Orientations of the [Cu(acac)(bipy)] or [Cu(acac)(Me_2bipy)] fragments:
(a) head-to-tail and (b) head-to-head orientation

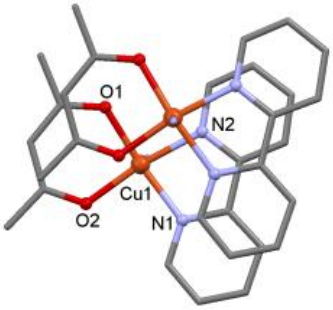
Overlap types **III** (3 hits) and **IV** (1 hit) are similar; both exhibit a head-to-head orientation; however, in contrast to overlap type **III,** overlap **IV** revealed a perfect face-to-face alignment and a non-parallel mutual stacking arrangement without offset (Figs. 6c, 6d) [23, 25, 49, 53]. The Cu···Cu distances are in a range of 3.920–4.699 Å.

Only one hit was found for type **V** overlap with a small overlapping area involving only the pyridine···pyridine moiety of bipy in stacking with Cu···Cu distances of 8.860 Å (Fig. 6e) [54]. A histogram of hit distribution over the different types of [Cu(acac)(bipy)] or [Cu(acac)(Me_2bipy)] overlap in the stacking is shown in Fig. 7).

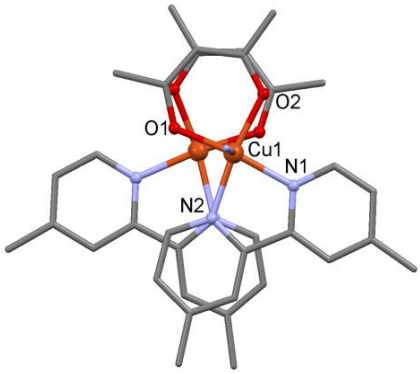
a) type **I** overlap



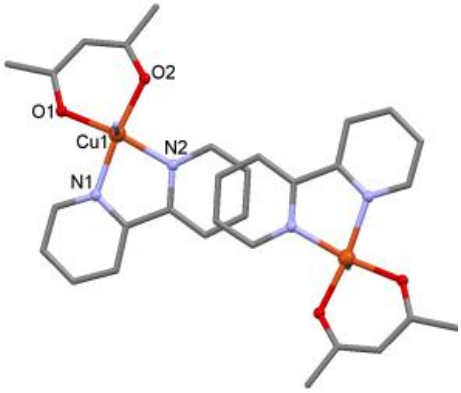
b) type **II** overlap



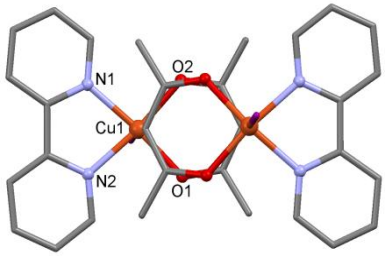
c) type **III** overlap



d) type **IV** overlap



e) type **V** overlap



f) type **VI** overlap

Fig. 6. The different types of overlap of [Cu(acac)(bipy)] or [Cu(acac)(Me_2bipy)] fragments in stacking; view perpendicular to the plane of the overlapping fragments.

Table 3. Parameters of stacking interactions in the structures of complexes with [Cu(acac)(bipy)] or [Cu(acac)(Me_2bipy)] fragments

Composition, Space group	overlap type	Centroid–centroid distances (Å)						P-to-P distance or angle (Å/°)*	Cu–Cu distance (Å)	Reference, refcode in CSD
		$d_{Py\text{-}Py}$	$d_{ac\text{-}py}$	$d_{ac\text{-}ac}$	$d_{ac\text{-}M}$	$d_{Py\text{-}M}$	$d_{M\text{-}M}$			
[{Cu(acac)(bipy)}$_2${Ni(CN)$_4$}], *P*-1	III	3.776	–	4.001	–	3.575	3.909	3.25	4.246	[25] DOZSIV
[Cu(acac)(bipy)(H_2O)]2[Ni(CN)$_4$], $P2_1/c$	II	3.653	4.216	–	3.808	–	3.928	3.420/3.405	3.950/7.410	[25] DOZSOB
[(Cu(acac)(Me_2bipy)]$_2$[Ni(mnt)$_2$], *P*-1	I	–	3.826	–	3.620	–	–	3.484	3.753	[25] DOZSUH
[Cu(acac)(bipy)Cl][Cu(acac)(bipy)(H_2O]Cl·H_2O, *P*-1	II, VI	3.829	–	3.310	–	–	–	3.064/2.95	7.617/5.105	[53] EBEDOG
[Cu(acac)(bipy)Br]H_2O, *P*-1	III	3.888	–	4.159	3.721	3.992	4.171	2.95	4.620	[53] EBEDUM
[Cu(acac)(Me_2bipy)(NCS)], *C*2/*c*	II, IV	3.825/ 3.591	–	3.325	–	4.053	–	3.494/2.2	7.547/3.920	[23] JAJSIX
[{Cu(acac)(Me_2bipy)(NCS)}$_2$Hg(SCN)$_2$], *P*-1	I, II	3.999	3.770	–	3.777	–	–	1.71/3.659	3.792/7.820	[23] JAJSUJ
[{Cu(acac)(bipy)}$_2$($\mu_{1,1}$-N_3)]$_3$(ClO_4)$_3$}·3.75H_2O, *P*-1	I, VI	3.713	–	3.354	–	3.691	3.465	3.156/1.51	5.191/5.275	[46] KEBYUM
[Cu(acac)(bipy)(H_2O)]NO_3}·H_2O, $P2_1/n$	III	–	–	–	3.551	–	–	2.04	4.699	[49] LIVNIO
[Cu(acac)(bipy)]BPh_4, *P*-1	I	–	4.125	–	3.500	–	–	3.538	3.570	[42] NEKCAJ
[Cu(acac)(bipy)(dmso)]BPh_4, *P*-1	I	–	3.682	–	3.995	–	3.726	3.243	4.192	[42] NEKDEO
[Cu(acac)(bipy)(dmf)](dmf) BPh_4, *P*-1	I	3.946	–	–	–	3.791	3.443	3.244	4.796	[42] NEKDIS
[Cu(acac)(bipy)(CH_3OH)] BPh_4, *P*-1	I	–	3.693	–	3.618		3.948	3.260	3.656	[42] NEKDOY
[Cu(acac)(bipy)(py)]BPh_4, *P*-1	I	–	3.487	–	–	4.102	–	3.264	4.588	[42] NEKDUE
[Cu(acac)(bipy)(py)]$_2$[Fe(CN)$_5$(NO)], *P*-1	V	3.798	–	–	–	–	–	3.477	8.860	[54] QAXHEC
[{Cu(acac)(bipy)}$_2$}{Ag(CN)$_2$}](ClO_4)·0.5CH_3CN, *P*-1	I	–	3.966	–	3.809	–	–	3.461	3.961	[43] RELROQ
[{Cu(acac)(bipy)}$_2$}{Au(CN)$_2$}](ClO_4)·0.5CH_3CN, *P*-1	II	3.766	–	–	–	–	–	0.39	7.516	[43] RELSAD
[Cu(acac)(bipy)I], *P*-1	VI	–	–	3.495	–	–	–	3.489	5.475	[55] VIKQUD

*interplanar distance or dihedral angle between about parallel planes.

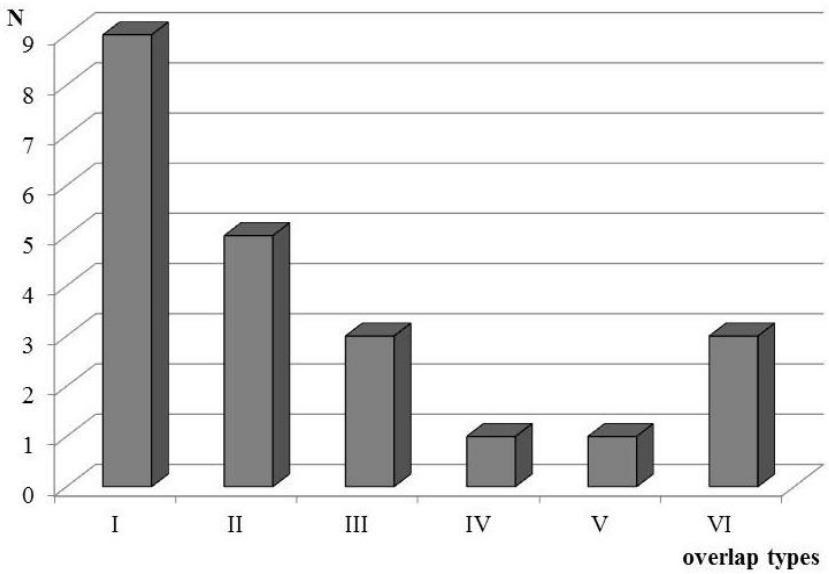


Fig. 7. Histogram of hit distribution over the different types of [Cu(acac)(bipy)] or [Cu(acac)(Me_2bipy)] overlap in the stacking.

The histogram in Fig. 7 and Table 3 show that metallacycles are not involved in stacking interactions (overlap types **II** and **V**) in only 3 from 18 analyzed structures (17%).

6. Conclusions

Analysis of the original results and literature data on square-pyramidal complexes of copper(II) containing a planar or about planar [Cu(acac)(AA)] fragment has revealed that the π–π stacking interaction between these fragments is the dominant intermolecular interaction in the structure of these complexes regardless of their cationic or neutral nature. Most often, metallacycles are involved in this interaction. Typically, an offset or slipped facial arrangement of the π-systems is observed. A head-to-head orientation of stacked fragments and a perfect face-to-face alignment of π-systems are rare. Stacking interactions between [Cu(acac)(AA)] fragments represent a reliable supramolecular synthon suitable to generate a robust supramolecular motif in the crystal structure.

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