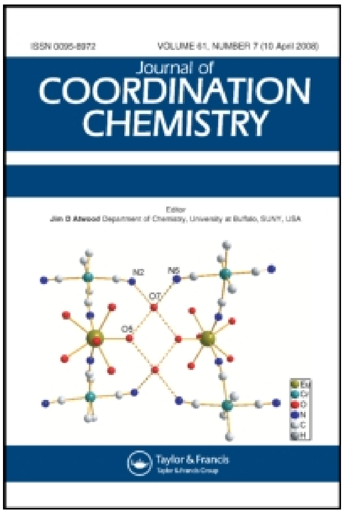

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Supramolecular organization in crystals containing quinoline-2-carboxylates and 9,10-dihydro-9-oxo-10-acridineacetates

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Supramolecular organization in crystals containing quinoline-2-carboxylates and 9,10-dihydro-9-oxo-10-acridineacetates

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Coordination compounds containing quinoline-2-carboxylate (quin-2-c) or 9,10-dihydro-9-oxo-10-acridineacetate ion (CMA) and ancillary ligands capable of hydrogen bond formation self assemble into 1D, 2D or 3D networks. The system of intermolecular hydrogen bonds that emerges depends mainly on the nature of the ancillary ligand. Aromatic–aromatic and C–H $\cdots\pi$ interactions are important forces for stabilizing crystal structures. Very strong stacking of aromatic heteropolycycles is found. An overview of complexes with quin-2-c and CMA is given and the organization of their crystal structures discussed.

Keywords: Quinoline-2-carboxylate; 9,10-Dihydro-9-oxo-10-acridineacetate; Crystal structures; Hydrogen bonds; Stacking interactions, C–H $\cdots\pi$ interactions; Supramolecular chemistry

1. Introduction

The study of supramolecular systems is important in chemistry, biology and medicinal and material sciences [1, 2]. Intermodular interactions leading to the formation of these systems can be weak as with hydrogen bonds [3, 4] or π–π stacking interactions [5, 6], or fairly strong as with metal–ligand bonds [7]. The formation of the metal–organic coordination networks is steered by the donor sets and geometries of the ligands and by the directionality of the coordination bonds formed. The use of the transition metals in the self-assembly process results in networks which can be finite (triangles, squares, etc.) [8–10] or infinite (1D, 2D or 3D networks) [11–13]. Whereas hydrogen bonded networks of coordination compounds have been well recognized [14], the role of aromatic–aromatic interactions in these compounds recently has gained growing attention [15–20].

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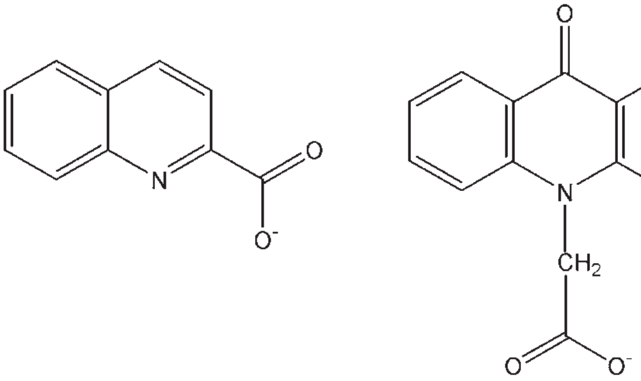

Scheme 1. Quinoline-2-carboxylate (left) and 9,10-dihydro-9-oxo-10-acridineacetate (right).

Carboxylate ligands are common in biological systems and in catalytic applications. The carboxylate group offers a variety of coordination modes and a great number of mono- and polynuclear complexes with this group has been obtained and characterized [21]. In this article we present an overview of coordination complexes with two carboxylate ligands bearing large heterocyclic substituents. The ligands are the quinoline-2-carboxylate (quin-2-c) and 9,10-dihydro-9-oxo-10-acridineacetate ions (CMA) (scheme 1).

Quinoline-2-carboxylate ion provides a donor set that mimics a fragment of the PQQ cofactor of the quionoprotein family [22]. The presence of the carboxylate group *ortho* to the quinoline nitrogen atom usually leads to five-membered chelate rings. In such cases the coordination sphere of the complex is often completed by solvent molecules or secondary ligands, which allow the formation of systems of hydrogen bonds. The uncoordinated oxygen atom from the carboxylate group acts as an acceptor in all complexes. The quinoline heterocycle of quin-2-c can participate in intermolecular π–π interactions. The sodium salt of 9,10-dihydro-9-oxo-10-acridineacetic acid (CMANa) is a very potent interferon inducer [23]. The peripheral 9-oxo oxygen atom in CMA offers the possibility of hydrogen bond formation [24] and the acridone ring system is suitable for π–π interactions [25].

In crystals of the complexes with both above mentioned ligands, a variety of intermolecular connections has been found and 1D, 2D or 3D structures are made by strong classical hydrogen bonds, $C–H\cdots O$ and $C–H\cdots\pi$ hydrogen bonds, and the π–π stacking. Analysis of the intermolecular contacts in the crystals of qui-2-c and CMA complexes has been made using published data and results generated in our laboratories.

2. Intermolecular interactions in the crystals of quinoline-2-carboxylates

Complexes of quin-2-c with metal ions are usually neutral molecules. In spite of the tendency of the quinoline-2-carboxylate ion to form the N,O-chelate rings with a monodentate bonded carboxylate group, several modes of quin-2-c coordination have been found; $\mu_2(O,O)$ bridging and chelating COO^- groups, as well as bonding of quin-2-c through monodentate carboxylate group are observed [26]. Hquin-2-c molecule as a zwitterion can bind to Sn(IV) through the oxygen atom [27]. Different coordination geometries are observed for the same molecular fragments depending on crystal composition. The secondary ligands indispensable for creation of hydrogen bonds are mainly water or alcohol molecules.

2.1. *Hydrogen-bonded coordination networks*

Linear assemblies of hydrogen bonded quinoline-2-carboxylates can be divided into three types, straight chains, zigzag chains and columnar structures. The straight chain configuration has been found in bis(ethanol)-bis(quinoline-2-carboxylato-N,O)-iron(II) (**1**) [28], bis(propanol)-bis(quinoline-2-carboxylato-N,O)-iron(II) (**2**) [29] and bis(ethanol)-bis(quinoline-2-carboxylato-N,O)-manganese(II) (**3**) [30] (figure 1a). Strong hydrogen bonds are made between hydroxyl groups of alcohols and the carboxylate group of quin-2-c, both coordinated to the metal.

An interesting example of a linear hydrogen bonded coordination network is found in benzimidazolium chloro-bis(quinoline-2-carboxylato)manganese(II) (**4**) [30]. Complex Mn(quin-2-c)$_2$Cl$^-$ anions are connected by benzimidazolium bridges (figure 1b). Bis(quinoline-2-carboxylato-N,O)-bis(imidazole)-manganese(II) (**5**) [31] forms a zigzag chain involving the carboxylate group of quin-2-c and the imine group of imidazole (figure 1c). The zigzag arrangement results from the *cis* configuration of

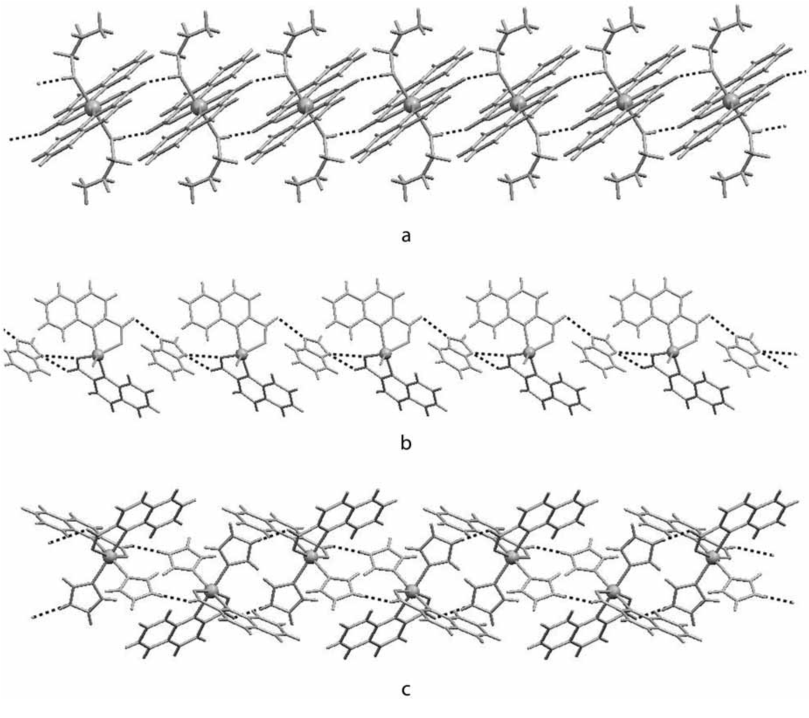

Figure 1. Straight chains of hydrogen bonded molecules in **2** (a) and in **4** (b); zigzag chain in **5** (c).

the ligands in **5**. The third type of 1D structure has been found in diaquaisothiocyanato-(quinoline-2-carboxylato-N,O)(quinoline-2-carboxylic acid-O)-manganese(II) (**6**) [32], bis(μ_2-quinoline-2-carboxylato-O,O,O′)-bis(triaqua-(quinoline-2-carboxylato-N,O)-(quinoline-2-carboxylato-O)-neodymium(III)) trihydrate (**7**) [27], *cis*-diaquabis(quinoline-2-carboxylato-N,O)-iron(II) quinoline-2-carboxylic acid monohydrate (**8**) [33] and *cis*-diaquabis(quinoline-2-carboxylato-N,O)-manganese(II) quinoline-2-carboxylic acid dihydrate (**9**) [30]. The system of hydrogen bonds involves the carboxylate group, coordinated and lattice water molecules and the carboxylic group creating a columnar, hydrophilic region surrounded by a hydrophobic border (figure 2).

There are two options for 2D structures made by hydrogen bonds in these compounds, planes [34–42] and layers [21]. A good example of a compound containing planes is diaquabis(quinoline-2-carboxylato-N,O)-manganese(II) (**10**) [34]. The inorganic plane in which all metal ions and hydrogen bonds are collected is shown in figure 3a. Layers constructed from a very complicated pattern of hydrogen bonds involving coordinated and lattice water molecules is observed in azido(quinoline-2-carboxylato-N,O)-triaquamanganese(II) monohydrate (**11**) [21] (figure 3b).

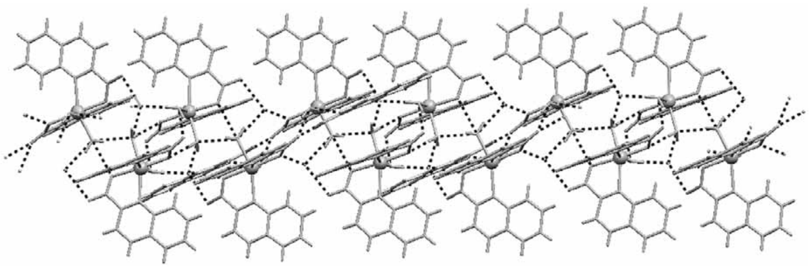

Figure 2. 1D columnar hydrogen bonded structure in **9**.

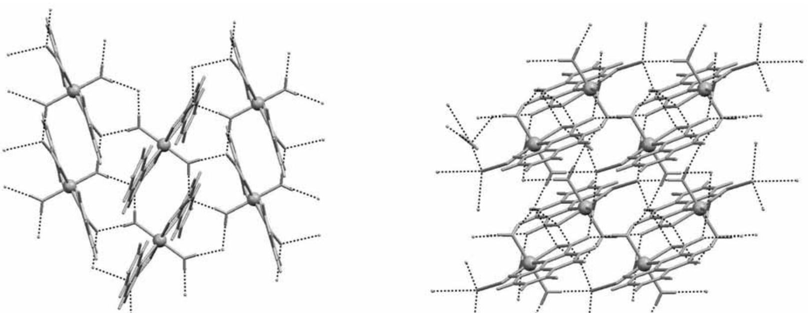

Figure 3. Plane resulting from the hydrogen bonds between carboxylate group and coordinated water molecule in **10** (a) and the layer created by hydrogen bonds between carboxylate groups, coordinated and lattice water molecules in **11** (b).

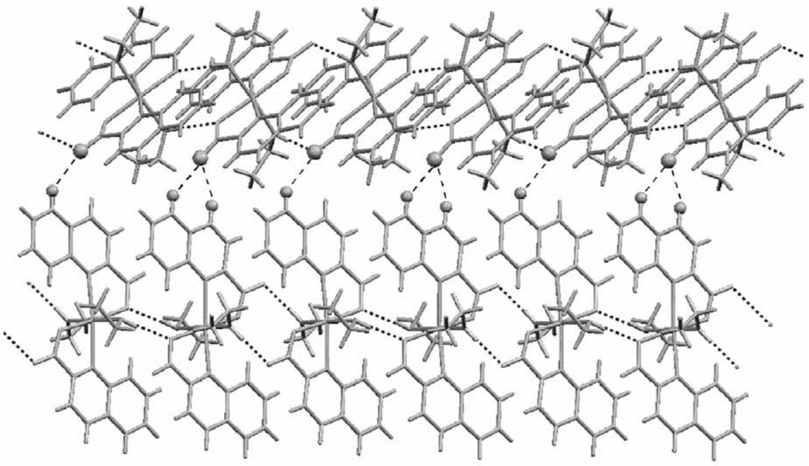

Figure 4. C–H $\cdots$ O bonds between 1D structure in **3**; oxygen and hydrogen atoms involved are marked.

2.2. *C–H $\cdots$ O interactions*

In many complexes of quin-2-c in the solid state, weak hydrogen bonds of the C–H $\cdots$ O type are observed. A non-coordinated oxygen atom of the carboxylate group is usually the acceptor, donors come from the quinoline rings, imidazole or from aliphatic groups. These bonds connect the 1D or 2D frameworks made by strong hydrogen bonds in cooperation with weaker π–π and C–H $\cdots$ π interactions. An example of such C–H $\cdots$ O bridges is shown in figure 4.

2.3. *Aromatic–aromatic and C–H $\cdots$ π interactions*

Various π–π interactions play important roles in crystals containing quinoline-2-carboxylates. The typical patterns of these interactions are stacks and the dimeric arrangement (figure 5). Stacks can be made of quinoline rings from coordinated quin-2-c ions as found in **11** (figure 5a). The second type of stack, in which molecules of the free acid, Hquin-2-c, participate, is observed in **8** and in **9** (figure 5b). More common in quinoline-2-carboxylates are π–π interactions between pairs of rings from coordinated ligands (figures 5c and 5d). Usually the ring planes are parallel, with distances between planes of 3.3–3.5 Å; the extent of overlap area is variable. According to Janiak [15], such contacts can be classified as being strong interactions. The π–π interactions often assemble the 1D networks into 3D structures. For example, in **9**, each columnar hydrogen bonded structure forms stacks with each of its four twin neighbours.

Although aromatic–aromatic contacts usually accompany the strongest hydrogen bonds in these compounds, there are examples in which the sole intermolecular forces stabilizing the crystals are π–π and C–H $\cdots$ π interactions. These include **12**, bis(1-methylimidazol-3-yl)-bis(quinoline-2-carboxylato-N,O)-zinc(II) (**13**) [43] (figure 6) and (μ_2-bis(diphenylphosphino)methane)bis(carbonyl-(quinoline-2-carboxylato-N,O)-rhodium) (**14**) [44]. In **13** the π–π and C–H $\cdots$ π contacts arrange the molecules in planes connected by C–H $\cdots$ O bonds. It is worth that, in spite of the lack of

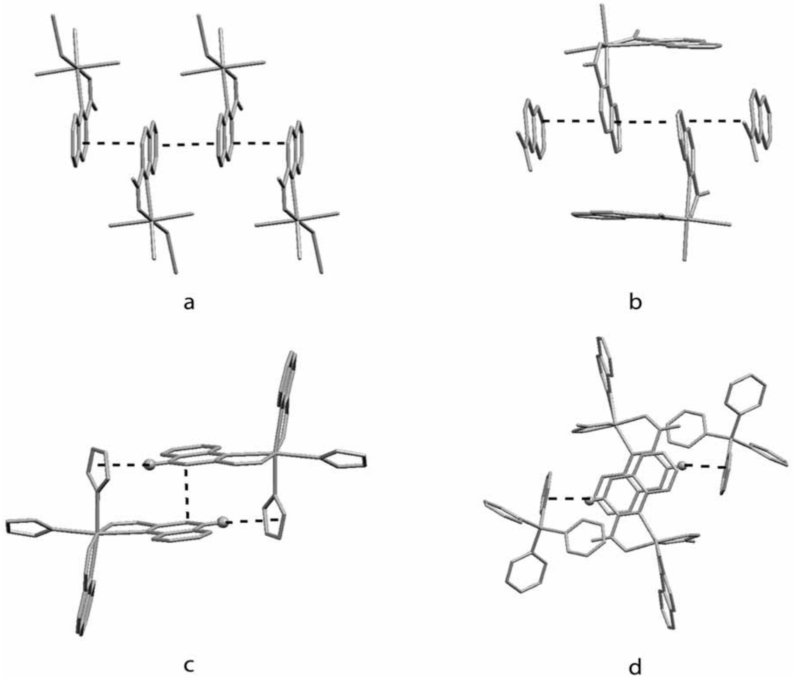

Figure 5. Staking arrangement in **11**(a); **9**(b); **5**(c); and **12**(d) from top to bottom, respectively.

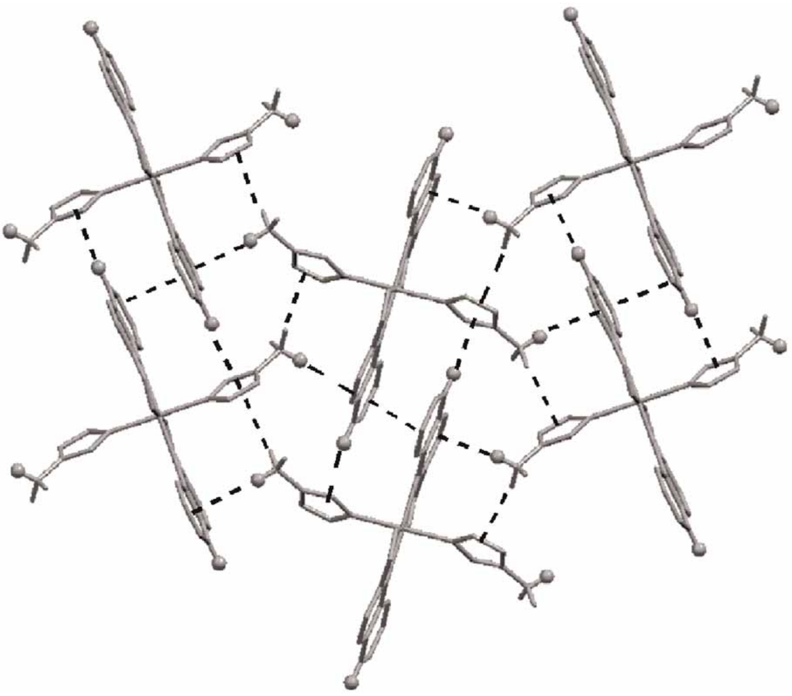

Figure 6. 2D motif due to π–π and C–H $\cdots$ π interactions in **13**.

strong hydrogen bonds in **13**, the structure is very compact, reflected by the relatively high density of the crystal, 1.537 g cm^{-3}.

Several types of C–H $\cdots \pi$ bonds have been found in the crystals containing quin-2-c. Interactions between aromatic C–H groups and imidazole rings in **5** and **13**, between aromatic C–H groups and phenyl rings in **12** and between aliphatic C–H groups and quinoline rings in **13** are observed. C–H $\cdots \pi$ contacts indicated in figures 5 and 6 satisfy criteria for such bonding very well [45, 46].

Effective cooperation between strong hydrogen bonds and π–π interactions is observed in diaquabis(quinoline-2-carboxylato-N,O)-manganese(II) diadenine (**15**) [47]. In **15** the inorganic planes comprising the metal ions and O–H $\cdots$ O bridges are separated by wide organic layers created by quinoline fragments of coordinated qui-2-c ligands and ribbons of adenine molecules. In the organic layer very extensive π–π interactions are found. Both inorganic and organic parts are connected by strong hydrogen bonds. In this case also the density of the crystal is high (1.625 g cm^{-3}) as compared to other manganese(II) complexes of quin-2-c.

3. Intermolecular interactions in 9,10-dihydro-9-oxo-10-acridineacetates

Six coordination compounds with CMA ligand have been obtained and structurally characterized. These are bis(9,10-dihydro-9-oxo-10-acridineacetato)bis(imidazole) bis(methanol)nickel(II) (**16**) [48], diaquabis(μ-9,10-dihydro-9-oxo-10-acridineacetato-*O*,*O*′:*O*)calcium (**17**) [49], diaquabis(μ-9,10-dihydro-9-oxo-10-acridineacetato-*O*,*O*′:*O*)lead(II) (**18**) [50], bis(9,10-dihydro-9-oxo-10-acridineacetato)bis(imidazole) copper(II) tetrahydrate (**19**) [50], diaquabis(μ-9,10-dihydro-9-oxo-10-acridineacetato-*O*)copper(II) (**20**) [51] and disodium tetra(9,10-dihydro-9-oxo-10-acridineacetato) zincate(II) bis(ethanol) heptahydrate (**21**) [52]. The CMA ligand binds to the metal through the carboxylate group in monodentate mode (**16**, **19**), as a chelate (**17**, **18**, **21**) and as a bridge (**17**, **18**, **19**, **21**). In complexes **16**–**21** the small neutral molecules capable of hydrogen bond formation complete the coordination spheres. Discrete units in **16** and **19** are monomers, in **17** and **18** dimers; **20** is a coordination polymer and in **21** a trinuclear mixed-metal cluster with a Na_2ZnO_3 core is found. Crystal architectures are dominated by strong hydrogen bonds and in all cases the 9-oxo oxygen atom participates to create the 1D, 2D or 3D structures. Strong aromatic–aromatic interactions are observed in crystals of the above compounds, with the exception of **19**.

A schematic view of **16** is shown in figure 7a. Each molecule forms four classical hydrogen bonds through imine groups from imidazoles and 9-oxo oxygen atoms. The resulting linear chains propagating along the *c* axis are connected by strong stacking interactions supported by C–H $\cdots$ O bonds into the 2D motif (figure 7b).

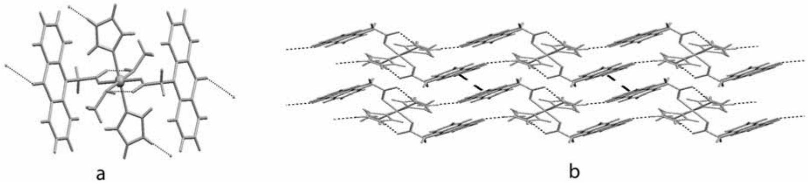

Figure 7. Molecular structure of **16**(a); hydrogen bonds to peripheral groups are indicated and chains of hydrogen bonded molecules are connected by π–π interactions (b).

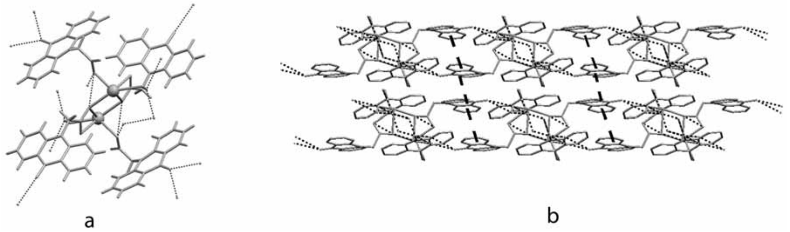

Figure 8. Molecular dimer **17**; hydrogen bonds to peripheral groups are indicated (a) and layers created by hydrogen bonds, intra- and inter-planar π–π interactions are indicated (b). Hydrogen atoms are omitted for clarity.

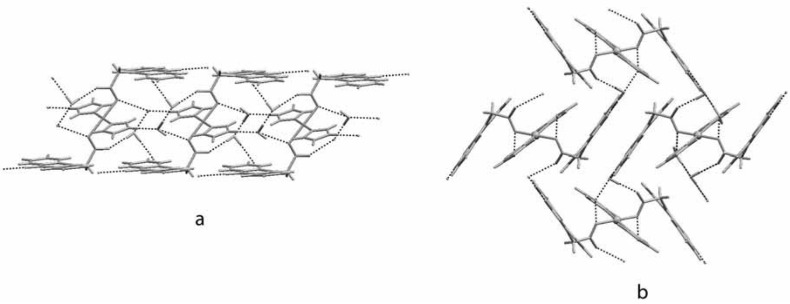

Figure 9. 1D (a); and 3D (b) structures created by hydrogen bonds in **19**.

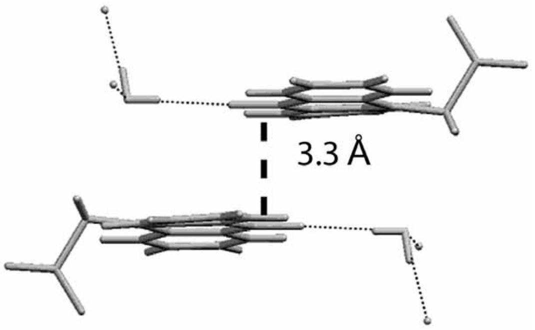

Figure 10. Interaction between hydrogen bonds and aromatic rings in **19**.

Discrete units in **17** and **18** are dimers, whose schematic structure is depicted in figure 8a. The dimers are collected in the layer due to strong hydrogen bonds and intra-layer stacking interactions (figure 8b). Inter-layer contacts of the aromatic–aromatic type lead to the 3D structure. Acridone rings are arranged parallel to each other in infinite stacks.

In **19** a 3D hydrogen bonded network is found. Figure 9a shows the linear motif built of monomers connected by strong hydrogen bonds and demonstrates the interchain contacts (figure 9b). Complex **19** is an exception among the 9,10-dihydro-9-oxo-10-acridineacetates because of the lack of stacking in the lattice. An interesting feature in **19** is the interaction between hydrogen bonds and aromatic rings (figure 10).

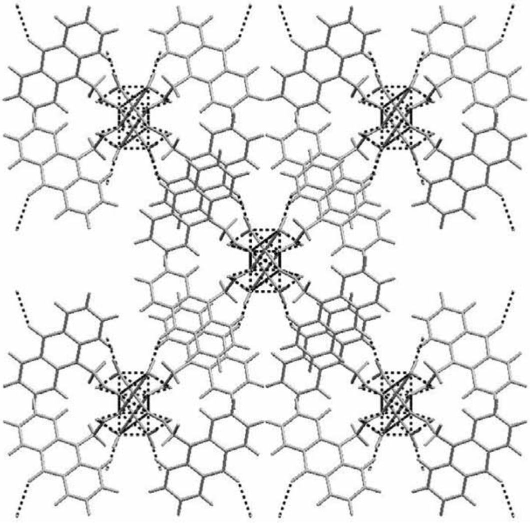

Figure 11. 3D structure in **20**; the coordination polymers are perpendicular to the figure plane and stacking interactions can be seen.

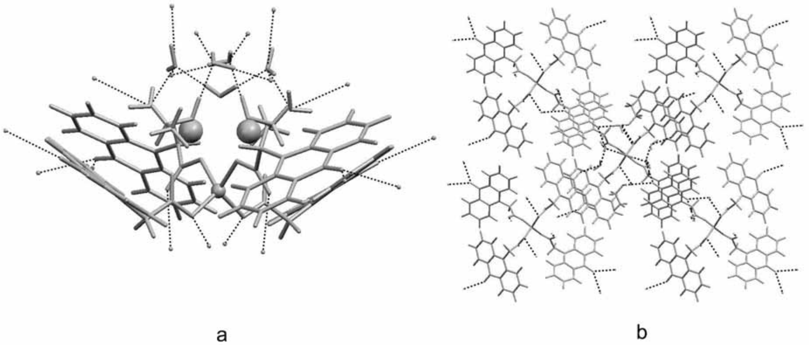

Figure 12. Molecular (a) and 3D structure (b) of **21**.

In this grouping, acridone rings are antiparallel, but do not overlap. The distance between the 9-oxo oxygen atom of a CMA ligand and the central CMA ring of a neighbouring molecule related by an inversion centre is very short, 3.3 Å. The 9-oxo oxygen atoms are the acceptors in strong hydrogen bonds with water molecules. Similar parallel stacking interactions between heterocycles involving hydrogen bonds have been recognized in protein crystals [5].

Complex **20** is the only example of a coordination polymer among the species discussed. Copper centres are connected by bridging carboxylate groups into zigzag chains. 3D structure in the lattice of **20** results from both O–H $\cdots$ O and C–H $\cdots$ O hydrogen bonds and stacking interactions (figure 11). The lattice of **21** is organized in a way similar to those observed in **6**, **7**, **8**, **9** and **20**. Hydrogen bonds propagate in three mutually perpendicular directions. Inorganic centres create the 1D motif, which is surrounded by acridone rings forming stacks. Figure 12a illustrates schematically the molecule of **21** and shows the packing in the crystal (figure 12b); hydrogen bonds are indicated and the overlap of acridone rings is notable.

The typical orientation of aromatic rings in complexes of CMA is a slipped-parallel mode. Ring planes are always almost parallel and distances between rings are very short, about 3.3 Å. The largest overlap is close to 60%. Such a strong aromatic–aromatic interaction is an important factor in the self-assembly processes [5, 15]. Only one C–H $\cdots\pi$ contact satisfying the criteria given by Steiner [45] is found; it involves the interaction of ethyl hydrogen atoms of one chain with imidazole rings of a parallel chain in **16**.

4. Summary and conclusions

The coordination compounds of transition metals with quinoline-2-carboxylate ion and 9,10-dihydro-9-oxo-10-acridineacetate ion form supramolecular structures in the solid state. In all discussed examples the coordination sphere around the metal ion is completed by small molecules, usually suitable for hydrogen bond formation. Cooperation between quin-2-c or; CMA with ancillary ligands enable the development of a variety of intermolecular interactions, resulting in 1D, 2D and 3D networks. These assemblies result from networks of classical hydrogen bonds, aromatic–aromatic and C–H $\cdots\pi$ interactions. The large heterocyclic substituents influence significantly the architecture of the crystals and strong stacking interactions are ubiquitous. Numerous C–H $\cdots$ O and C–H $\cdots\pi$ contacts stabilize crystals of quin-2-c complexes. In conclusion, it is noted that that all syntons identified in organic crystal engineering research apply to networks of coordination compounds. Stable crystal lattices of complex molecules can be assembled solely due to very weak π–π and C–H $\cdots\pi$ bonds.

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