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Metal complexes as second-sphere ligands

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Novel supercomplexes are constructed from a mononuclear square planar Ni(II) or Pd(II) complex acting as a host receptor towards the aqua ligand from copper complexes.

The systematic investigation and deliberate construction of the second coordination sphere, based upon non-covalent interactions of the first-sphere ligands with neutral or charged species, represent an active area of research in metallosupramolecular chemistry.[1] Originating from Alfred Werner's classical works on coordination chemistry, the concept of second-sphere coordination is nowadays illustrated by a large variety of "complexes of complexes".[2–4] Crown ethers and macropolycyclic ethers have been widely employed as host receptors, while the guests are metal complexes containing hydrogen-bond donor groups (*e.g.* NH_3, H_2O).[2–5] Aromatic crown ethers can interact not only through the oxygen atoms, as hydrogen-bond acceptors, but also through the aromatic rings, which can be involved in π–π stacking interactions with the aromatic ligands coordinated to the metal ion. The classical examples are the supercomplexes resulting from the interaction of $[Pt(bipy)(NH_3)_2]^{2+}$ with the dibenzo-3*n*-crown-*n* family ($n = 6–12$).[6] Cyclodextrins and cyclophanes have also been employed as second-sphere ligands, by exploiting the ability of their cavities to interact with, respectively, hydrophobic and π-electron rich guests.[3] Very nice examples are based upon bifunctional ligands, namely organic molecules which interact by means of one functional group with the metal ion, and, by means of the other (containing hydrogen-bond donor and/or acceptor groups), with molecules containing complementary arrangements of the hydrogen-bond donors and acceptors.[7] By using the second coordination sphere, it was possible to construct more sophisticated architectures, such as rotaxanes.[8]

Here we report on a rational construction of the second coordination sphere, which is based on the observation that mononuclear complexes obtained by using bicompartmental ligands should act as hosts by exploiting the free compartment. Such a ligand is the dianion of the Schiff-base resulting from the 2 : 1 condensation of 3-methoxysalicylaldehyde with ethylenediamine, L^{2-}. The reaction between $PdCl_2$ or $NiCl_2$ and the organic ligand, in a 1 : 1 molar ratio, leads to the neutral mononuclear complexes, [Pd(L)] and [Ni(L)] respectively, in which the metal ion is located in the N_2O_2 compartment (Scheme 1). As guests we used copper(II) complexes from a family intensively investigated in our laboratory, $[Cu(AA)(BB)(H_2O)](ClO_4)$ (AA = acetylacetonato; BB = 2,2′-bipyridine, 1,10-phenanthroline).[9] The water molecule coordinated to the apical position of the copper ion can interact through hydrogen bonds with the oxygen atoms from the free compartment of the [Pd(L)]/[Ni(L)] complex. Moreover, the stability of the resulting complex of complexes can be reinforced by π–π stacking interactions established between the aromatic rings of the Schiff base and the organic ligands attached to the copper ion (Scheme 2).

The slow evaporation of a solution (methanol–acetonitrile) containing [Pd(L)] or [Ni(L)] and $[Cu(acac)(bipy)(H_2O)](ClO_4)$ or $[Cu(acac)(phen)(H_2O)](ClO_4)$ complexes leads to the cocrystallization of the two components.† Crystallographic investigation of the green crystals reveals the formation of the targeted supercomplexes: $\{[Cu(acac)(bipy)(H_2O)][Pd(L)](ClO_4)\}$ **1**, $\{[Cu(acac)(phen)(H_2O)][Pd(L)](ClO_4)\}$ **2** and $\{[Cu(acac)(phen)(H_2O)][Ni(L)](ClO_4)\}$ **3**.‡ The three systems are isomorphous, and only the crystal structure of **3** will be discussed here. Each individual mononuclear complex exhibits its expected characteristic features. The nickel (palladium) ion displays a square-planar coordination geometry, with the nickel (palladium) ion coordinated into the N_2O_2 compartment of the Schiff-base ligand. The Ni–O and Ni–N bond lengths are: Ni(1)–O(2) = 1.864(3), Ni(1)–O(3) = 1.851(3); Ni(1)–N(1) = 1.824(5), Ni(1)–N(2) = 1.856(4) Å. The copper(II) ions are pentacoordinate with a square-pyramidal geometry. The basal plane is formed by the oxygen and nitrogen atoms arising from the organic ligands, with the Cu–O bonds [1.912(3) Å] shorter than the Cu–N ones [1.998(4); 2.004(3) Å]. The apical position is occupied by the aqua ligand [Cu(1)–O1W = 2.261(3) Å].

The two complementary mononuclear complexes generate supramolecular units by convolution of two types of non-covalent forces: hydrogen bonding and π–π interactions. The aqua ligand from the copper complex is hydrogen bonded to the oxygen atoms from the free compartment of the nickel (palladium) complex [H(1W)···O(1) = 1.851, H(1W)···O(2) = 2.221, H(2W)···O(3) = 2.215, H(2W)···O(4) = 2.128 Å] (Fig. 1). Strong π–π stacking interactions (3.4–3.5 Å) occur between the phenyl rings of the Schiff-base and the phenanthroline ligand from the copper complex (Fig. 2).

The packing of the supramolecular dimers in the crystal can be rationalized as well: it is mainly driven by the stacking interactions involving the phenanthroline ligand from one dimer and the phenyl rings of the Schiff-base from another one. Indeed, the analysis of the packing diagrams reveals the formation of supramolecular chains, running along the

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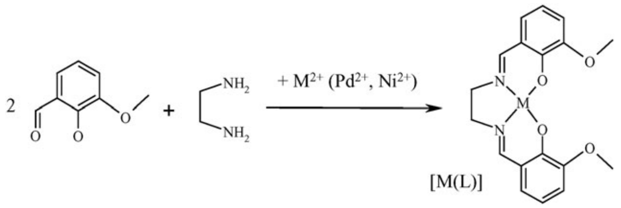
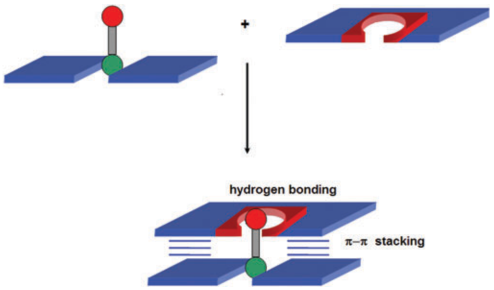


Scheme 1



Scheme 2

crystallographic *c* axis, sustained by π–π aromatic interactions (3.4–3.5 Å) (Fig. 3).

The solution (methanol–acetonitrile, 1 : 1) UV–VIS spectrum of the mononuclear copper(II) complex [Cu(acac)(phen)(H_2O)](ClO_4) exhibits a large band with the maximum located at 600 nm. The interaction with the nickel (or palladium complex) causes a small shift towards lower wavelengths, very likely as a result of the weak perturbation of the crystal field experienced by the copper(II) ion, thus indicating that the association observed in the solid state takes place also in the solution.

Conclusion

The examples we presented herein illustrate a rational way in constructing the second coordination sphere of a metal complex. They also bring new insights into the understanding of the co-crystallization processes. Our approach is based on the use of square-planar mononuclear Ni(II) or Pd(II) complexes, with bicompartmental ligands, whose free compartment acts as a receptor for the aqua ligand arising from a second complex. The peculiarities of the organic ligands allow one to predict the packing of the two complexes in the crystal.

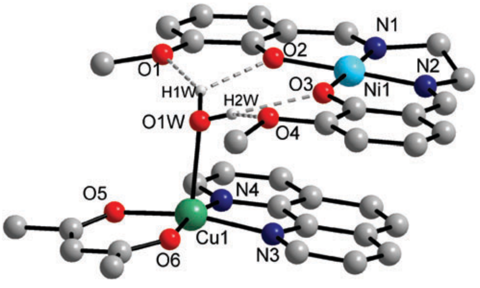


Fig. 1 View of the supramolecular unit {[Cu(acac)(phen)(H_2O)][NiL]}$^+$ in crystal **3**, showing the formation of the hydrogen bonding.

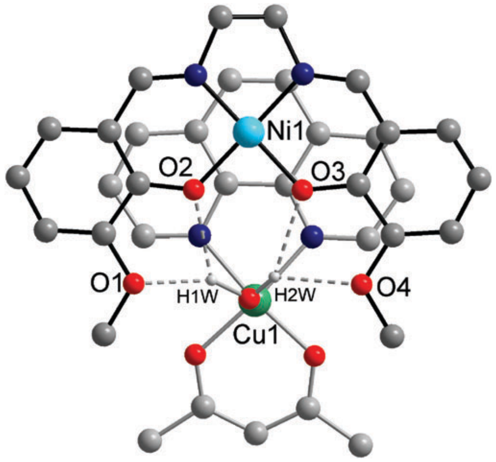


Fig. 2 View of the supramolecular unit {[Cu(acac)(phen)(H_2O)][NiL]}$^+$ in crystal **3**, showing the π–π interactions.

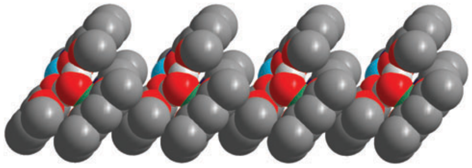


Fig. 3 Packing diagram in crystal **3** showing the formation of the supramolecular chains. Colour code: light blue: nickel; green: copper; red: oxygen; dark grey: carbon; light grey: hydrogen.

Acknowledgements

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† Syntheses: the [Cu(acac)(phen)(H_2O)](ClO_4) and [Cu(acac)(bipy)(H_2O)](ClO_4) mononuclear complexes were obtained as already reported.[9] The [Pd(L)] and [Ni(L)] mononuclear complexes: 5 mmol $PdCl_2$, $NiCl_2$ respectively, were added to an ethanolic solution (20 mL) of 3-methoxysalicylaldeyde (10 mmol), ethylenediamine (5 mmol) and triethylamine (5 mol). The mixture was boiled during 15 min. The precipitate that resulted on cooling was filtered off and washed with ethanol and diethyl ether. The compounds {[Cu(acac)(bipy)(H_2O)][Pd(L)](ClO_4)} (**1**), {[Cu(acac)(phen)(H_2O)][Pd(L)](ClO_4)} (**2**) and {[Cu(acac)(phen)(H_2O)][Ni(L)](ClO_4)} (**3**) were obtained following the same procedure: 10 mL solution (acetonitrile) containing 0.1 mmol [Cu(acac)(bipy)(H_2O)](ClO_4) for **1**, and [Cu(acac)(phen)(H_2O)](ClO_4) for **2** and **3** respectively, were added to 15 mL methanolic solution containing 0.1 mmol [Pd(L)] (for **1** and **2**) or [Ni(L)] (for **3**). The green crystals of **1**, **2** and **3** were obtained by slow evaporation at room temperature of the resulting mixtures.

‡ Crystallographic data for **1**: $C_{33}H_{35}Cl_1CuN_4O_{11}Pd_1$, $M = 869.04$ g mol^{-1}, monoclinic, space group $P2_1/c$, $a = 11.9832(10)$ Å, $b = 36.0090(32)$ Å, $c = 8.4136(6)$ Å, $\beta = 105.4805(5)^\circ$, $V = 3498.8(5)$ Å^3, $Z = 4$, $T = 293$ K, $D_c = 1.648$ g cm^{-3}, $\mu = 1.2363$ mm^{-1}, $R_1 = 0.0670$, $wR_2 = 0.1201$, GooF = 1.005; for **2**: $C_{35}H_{33}Cl_1CuN_4O_{11}Pd_1$, $M = 891.04$ g mol^{-1}, monoclinic, space group $P2_1/c$, $a = 12.5433(11)$ Å, $b = 35.5247(25)$ Å, $c = 8.4370(8)$ Å, $\beta = 105.647(6)^\circ$, $V = 3620.2(5)$ Å^3, $Z = 4$, $T = 293$ K, $D_c = 1.635$ g cm^{-3}, $\mu = 1.224$ mm^{-1} , $R_1 = 0.0706$, $wR_2 = 0.1094$, GooF = 0.945; for **3**: $C_{35}H_{35}Cl_1CuN_4O_{11}Ni_1$, $M = 845.37$ g mol^{-1}, monoclinic, space group $P2_1/c$, $a = 12.6386(12)$ Å, $b = 35.110(2)$ Å, $c = 8.4367(6)$ Å, $\beta = 106.723(10)^\circ$, $V = 3585.4(5)$ Å^3, $Z = 4$, $T = 293$ K, $D_c = 1.566$ g cm^{-3}, $\mu = 1.259$ mm^{-1}, $R_1 = 0.0382$, $wR_2 = 0.0545$, GooF = 0.757. X-Ray diffraction measurements were

performed on a Kappa CCD diffractometer for **1** and **2**, and on a STOE IPDS diffractometer for **3**, using graphite-monochromated MoKα radiation ($\lambda = 0.71073$ Å). The structures were solved by direct methods and refined by full-matrix least squares techniques based on F^2. The non-H atoms were refined with anisotropic displacement parameters. Calculations were performed using SHELX-97 crystallographic software package. CCDC reference numbers: 293152–293154. For crystallographic data in CIF or other electronic format see DOI: 10.1039/b517989k

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