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Solvent-modulated reversible conversion of a [2 × 2]-grid into a pincer-like complex

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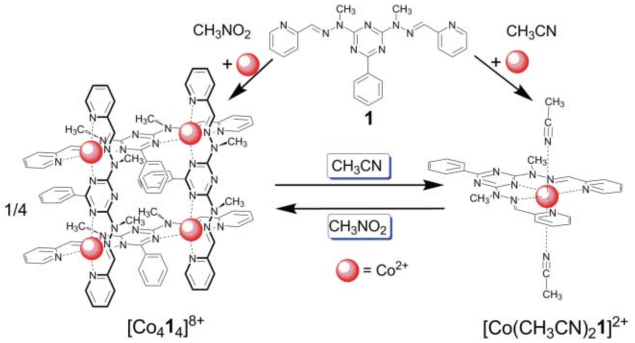
The triazine derived ligand 1 reacts with one equivalent of Co(II) salts to give complexes whose architecture depends on the solvent employed: the [2 × 2]-grid like tetranuclear complex and the pincer-like mononuclear complex, obtained respectively by crystallization from nitromethane and from acetonitrile may be interconverted reversibly, the grid-pincer conversion being markedly accelerated by adding an amine.

The influence of the medium on the organization of supramolecular systems[1] covers a wide area. Thus, solvent modulated molecular folding or unfolding is a phenomenon which has important consequences, for example in denaturation of proteins with dramatic changes in their biological activity.[2] Synthetic systems also may show solvent dependence of their properties, such as the solvent dependent assembly of an oligocarboxamide strand into a single or a double helix,[3] the generation of either a square or a hexagonal complex,[4] the formation of either a double or a single helical silver(I) complex,[5] solvent-dependent peptide-based molecular shuttles,[6] solvent-induced adaptive behaviour of switchable chiral architectures containing Pr(III) ions[7] *etc.* Such processes are of much interest in the framework of constitutional dynamic chemistry,[8,9] as they represent an adaptive response of a (metallo)supramolecular architecture to environmental changes through a change in constitution. We report herewith a system in which the reversible conversion of a grid-like[10] into a pincer-like[11] complex is modulated by the nature of the solvent (Scheme 1).



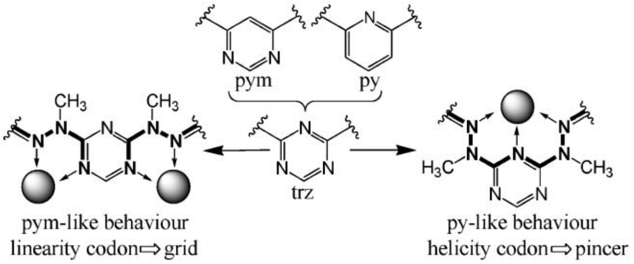
Scheme 1 Solvent modulated reversible conversion of the grid into the pincer-like complex (for details, see text).

It is well established that ligands containing two terpyridine-type subunits based on a central pyrimidine (pym) group form [2 × 2] tetranuclear grid-type metallo-architectures.[10] Replacement of the pym unit by a triazine ring introduces a third nitrogen center that may serve as further metal ion binding site and markedly modify the coordination properties of the ligand. Thus, in the ligand **1**, obtained by condensation of 2-pyridinecarbaldehyde (2 equiv.) with bis(methylhydrazino)phenyltriazine (1 equiv.), in ethanol (75% yield, m.p. 231 °C),[12] the disubstituted triazine unit can be seen as the combination of a 4,6-disubstituted pyrimidine (pym) and of a 2,6-disubstituted pyridine (py) (Scheme 2). Consequently, the triazine (trz) central unit of ligand **1** may act, on coordination of Co(II) ions, both as a two-site pym or as a single-site py unit, leading to two different complexes containing the coordinated ligand **1** either in a linear ($[Co_4\mathbf{1}_4]^{8+}$) or in a bent, helical-type ($[Co(CH_3CN)_2\mathbf{1}]^{2+}$) shape.

Ligand **1** presents the coordination plasticity required for undergoing structural adaptation in response to environmental triggers (Scheme 2).

Ligand **1** was reacted with $Co(BF_4)_2{\cdot}6H_2O$ tetrafluoroborate in CH_3NO_2, at room temperature (Scheme 1). The solution was introduced into crystallization tubes and diffusion of $CHCl_3$ as non-solvent led to red crystals. The ^1H NMR spectrum of these crystals dissolved in CD_3NO_2 showed the presence of a paramagnetic complex whose signals display chemical shifts ranging from −40 to 70 ppm (Fig. 1(a)). The solid-state molecular structure determined by X-ray crystallography† indicated that the species formed were a [2 × 2]-grid type complex[10] $[Co_4\mathbf{1}_4](BF_4)_8$ composed of four ligands and four Co(II) ions in an octahedral coordination geometry (Fig. 2(a)).

Starting from ligand **1** and $Co(ClO_4)_2{\cdot}6H_2O$ and using CH_3CN as a solvent, a different complex was crystallized by diffusion of $(C_2H_5)_2O$ as non-solvent and its solid-state molecular structure was determined by X-ray crystallography. It was found to be the mononuclear helical pincer-like complex $[Co(CH_3CN)_2\mathbf{1}](ClO_4)_2$



Scheme 2 Disubstituted triazine unit seen as a combination of linearity and helicity codons generated on complexation of appropriate metal ions.

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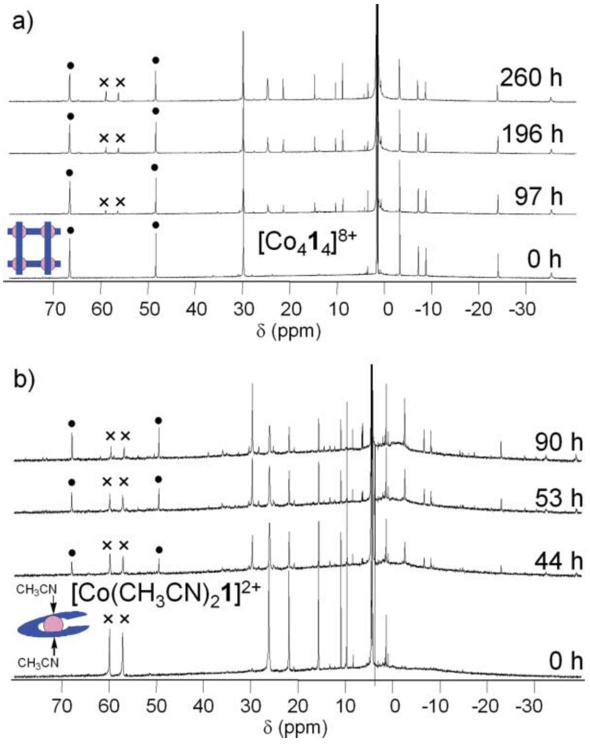

Fig. 1 ^1H NMR spectra (400 MHz) of the conversion of the grid $[Co_4\mathbf{1}_4]^{8+}$ (•) into the pincer like complex $[Co\mathbf{1}]^{2+}$ (×), in CD_3CN, at 55 °C (a) and of the pincer $[Co\mathbf{1}]^{2+}$ (×) into the grid-like complex $[Co_4\mathbf{1}_4]^{8+}$ (•), in CD_3NO_2, at 70 °C (b).

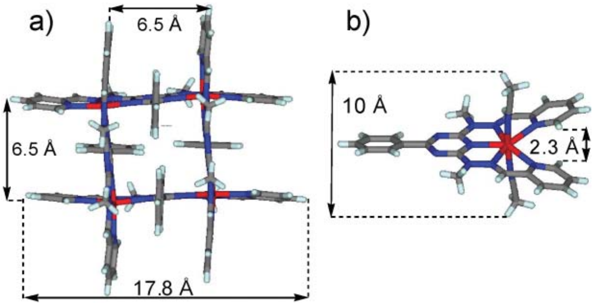

Fig. 2 Solid-state molecular structure of the grid-like $[Co_4\mathbf{1}_4](BF_4)_8$ (a) and pincer-like $[Co(CH_3CN)_2\mathbf{1}](ClO_4)_2$ (b) complexes; anions and solvent molecules are omitted for clarity. Centroid-to-centroid distances (Å) are represented.

(Fig. 2(b)) in which the Co(II) cation is coordinated by five nitrogen atoms of the ligand (two N sites from py, two sp^2 hydrazone N sites and the N5 site of the central triazine) and by two nitrogen sites from two molecules of acetonitrile. The ^1H NMR spectrum presents signals of chemical shifts ranging from 0 to 60 ppm, in agreement with its paramagnetic nature (Fig. 1(b)).

Direct observation by ^1H NMR of the solution resulting from the reaction of ligand **1** with $Co(BF_4)_2{\cdot}6H_2O$ in CD_3NO_2 showed the presence of both the grid and the pincer-type complexes in about equal amounts. On the other hand, similar direct observation in CD_3CN showed the formation of only the pincer species. The formation of both species in CD_3NO_2 is probably due to coordination of water molecules to the axial sites of the cobalt centre (see also below).

The Co–N distances in the grid $[Co_4\mathbf{1}_4](BF_4)_8$ are shorter than those in the pincer $[Co(CH_3CN)_2\mathbf{1}](ClO_4)_2$, in accordance with the fact that the coordination is stronger in the grid, due to the octahedral geometry generated by the two tridentate subunits, while in the pincer-like complex the Co(II) is hepta-coordinated and steric repulsion between the ends of the ligand may force it to adopt a twisted conformation (distances (Å) $Co–N_{hyz}$/$Co–N_{py}$/$Co–N_{trz}$ in $[Co_4\mathbf{1}_4](BF_4)_8$: 2.089/2.141/2.191; in $[Co(CH_3CN)_2\mathbf{1}](ClO_4)_2$: 2.267/2.280/2.190).

Electrospray mass spectrometry (ES-MS) agreed with the crystallographic determinations.[13]

The formation of two different complexes depending on the solvent used, led us to investigate their interconversion starting from pure crystallized entities.

Upon dissolution of crystals of $[Co_4\mathbf{1}_4](BF_4)_8$ grid in acetonitrile, a slow partial conversion ($\approx$25% after 11 days at 55 °C) into the pincer $[Co(CH_3CN)_2\mathbf{1}]^{2+}$ was observed by ^1H NMR spectroscopy. A reverse pincer-to-grid conversion ($\approx$70% after 4 days at 70 °C) was observed by dissolving crystals of $[Co(CH_3CN)_2\mathbf{1}](BF_4)_2$ in nitromethane (Fig. 1(b)).

This type of solvent-depending structural interconversion can be understood taking into account the dual coordinative behaviour of the ligand (Scheme 2), modulated by the stronger coordinative aptitude of acetonitrile with respect to nitromethane. The formation of the grid takes place in a solvent of low coordinative capacity, allowing the coordination of Co(II) solely by the ligand **1** and thus the assembly of the tetranuclear complex. On the other hand, the stronger coordination ability of acetonitrile molecules stabilizes the pincer by binding to the cobalt(II) center.

A related process occurs in the interconversion of a grid structure an a hexanuclear hexagonal architecture.[4] However, it should be noted that in this former case the conformation of the coordinated ligand remains unchanged when passing from the grid to the hexagon (the geometry codon is the same), while in the present case the dual nature (Scheme 2) of ligand **1** provides coordinative plasticity that allows the interconversion between the linearity and helicity codons.

One may expect that an agent of more pronounced coordination ability than CH_3CN would accelerate the grid to pincer conversion by facilitating dissociation of the former and stabilizing the latter by binding to its Co(II) center. Thus, it is likely that addition of a primary amine to a solution of $[Co_4\mathbf{1}_4]^{8+}$ in CH_3CN would generate an amine-pincer complex having the same structure as $[Co(CH_3CN)_2\mathbf{1}]^{2+}$ with the two CH_3CN molecules replaced by coordinated amine molecules (Fig. 3). Indeed, adding 8 equiv. of propylamine $^nPrNH_2$ to a grid solution in CD_3CN, induced complete conversion into the amine-pincer $[Co(^nPrNH_2)_2\mathbf{1}]^{2+}$ within about 1 day at 55 °C and 15 min at 80 °C (Fig. 3). Subsequent addition of 8 equiv. of CF_3SO_3H to this solution caused the protonation of the amine, leading to $[Co(CH_3CN)_2\mathbf{1}]^{2+}$, presenting the same NMR spectrum as the isolated complex. When the same experiment is performed in CD_3NO_2 solution, the addition of 8 eq. $^nPrNH_2$ disrupts the grid and subsequent addition of 8 eq. CF_3SO_3H restores it, the intermediate being however different from $[Co(^nPrNH_2)_2\mathbf{1}]^{2+}$ as there is no acetonitrile present.

Thus, the interconversion between the two species may be modulated not only by the medium itself, but also by additives capable of coordinating to the two axial sites of the pincer complex. Indeed, direct reaction of ligand **1** with

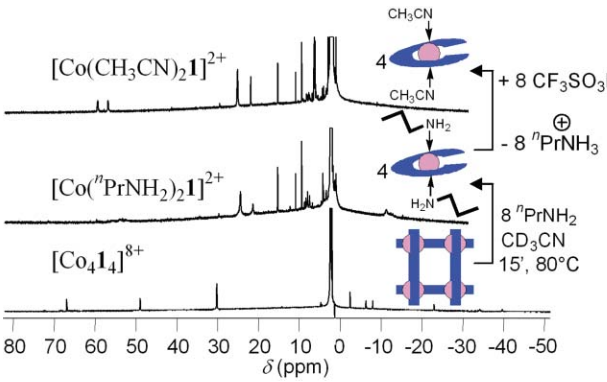

Fig. 3 ^1H NMR spectra (400 MHz, CD_3CN) for the possible mechanism for amine mediated conversion of grid $[Co_4\mathbf{1}_4]^{8+}$ into the pincer $[Co(CH_3CN)_2\mathbf{1}]^{2+}$ passing through the amine-coordinated pincer intermediate $[Co(^{n}PrNH_2)_2\mathbf{1}]^{2+}$.

$[Co(DMSO)_6(BF_4)_2]$,[14] in CD_3NO_2 led only to the pincer-like complex, presumably due to the coordination of DMSO molecules to the cobalt centre. Thus, the presence of accessible axial sites in the pincer complex but not in the grid species offers another handle on controlling the system.

To summarize, the couple $[Co_4\mathbf{1}_4]^{8+}/[Co(CH_3CN)_2\mathbf{1}]^{2+}$ represents a system of two solvent-interconvertible paramagnetic Co(II) complexes and implements three features: (i) adaptation to external/medium effects, (ii) dual ligand structural plasticity and (iii) effector-induced facilitation of structural interconversion. Further investigations concerning the behaviour of other metal ions and of related systems presenting constitutional dynamic behaviour are ongoing.

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Notes and references

† *Crystallographic data* (T = 173 K, radiation Mo-Kα = 0.71073 Å). $[Co_4\mathbf{1}_4](BF_4)_8$: $[Co_4(C_{23}H_{21}N_9)_4](BF_4)_8\cdot 10CH_3NO_2$; M = 3234.59; crystal system: tetragonal; space group: $P42/n$ (no. 86); a = 17.2360(4), c = 24.4290(4) Å; V = 7257.4(3) Å^3; Z = 2; D_c = 1.376 g cm^{-3}; μ = 0.546 mm^{-1}; $F(000)$ = 2964; 1.5° $\leqslant \theta \leqslant$ 30.0°; *hkl* limits: −24/24, −17/17, −27/34; number of data measured: 19072; number of data with $I > 2\sigma(I)$: 6475; R = 0.1225. $[Co(CH_3CN)_2\mathbf{1}](ClO_4)_2$: $[Co(CH_3CN)_2(C_{23}H_{21}N_9)](ClO_4)_2$; M = 763.43; crystal system: monoclinic; space group: $C2/c$ (no. 15); a = 15.542(4), b = 16.699(4), c = 13.539(3) Å; β = 112.93(2)°; V = 3236.2(14) Å^3; Z = 4; D_c = 1.567 g cm^{-3}; μ = 0.762 mm^{-1}; $F(000)$ = 1564; 2.1° $\leqslant \theta \leqslant$ 27.5°; *hkl* limits: 0/20,0/21,17/16; number of data measured: 3679; number of data with $I > 2\sigma(I)$: 2528; R = 0.0488. CCDC 609649 and 609650. For crystallographic data in CIF or other electronic format see DOI: 10.1039/b612222a

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12 NMR data for ligand **1**: ^1H NMR ($CDCl_3$, 400 MHz, reference: solvent residual peak, δ 7.24 ppm): 8.62 (d, J = 4.4 Hz, 2H), 8,58 (d, J = 7 Hz, 2H), 8.33 (d, J = 7.7 Hz, 2H), 8.08 (s, 2H), 7.79 (td, J = 7.3, 1.5 Hz, 2H), 7.59–7.49 (m, 3H), 7.29 (ddd, J = 7.3, 4.8, 1.1 Hz, 2H), 3.88 (s, 6H) ppm; ^{13}C NMR ($CDCl_3$, 100 MHz, reference: solvent residual peak, δ 77.2 ppm): 154.7, 149.4, 140.8, 136.5, 136.5, 132.4, 129.0, 128.6, 123.8, 120.6, 31.2 ppm. Bis(methylhydrazino)phenyltriazine (mp 155 °C) was prepared in 40–50% yield by reflux of methylhydrazine (4 equiv.) with 2,4-dichloro-6-phenyltriazine (R. Menicagli, S. Samaritani and V. Zucchelli, *Tetrahedron*, 2000, **56**, 9705), in ethanol, during 2 h. See: J.-L. Schmitt, PhD Thesis, Université Louis Pasteur, Strasbourg, 2004.

13 (*a*) ES-MS for $[Co\mathbf{1}](ClO_4)_2$: a peak corresponding to $[Co\mathbf{1}]^{2+}$ (m/z calc. for $[CoC_{23}H_{21}N_9]^{2+}$: 241.0620, found: 241.0624); (*b*) ES-MS for $[Co_4\mathbf{1}_4](ClO_4)_8$: peaks corresponding to $\{[Co_4\mathbf{1}_4](ClO_4)_6\}^{2+}$ (m/z calc. for $[Co_4C_{92}H_{84}N_{36}Cl_6O_{24}]^{2+}$: 1263.0945, found: 1263.0826), $\{[Co_4\mathbf{1}_4](ClO_4)_5\}^{3+}$ (m/z calc. for $[Co_4C_{92}H_{84}N_{36}Cl_5O_{20}]^{3+}$: 808.4137, found: 808.4103), $\{[Co_4\mathbf{1}_4](ClO_4)_4\}^{4+}$ (m/z calc. for $[Co_4C_{92}H_{84}N_{36}Cl_4O_{16}]^{4+}$: 581.5731, found: 581.5747).

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