

Condensation of acetonitrile into *N*-acetimidoylacetylamine promoted by a dinuclear nickel(II) complex†‡

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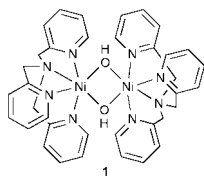
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Acetonitrile reacts with a dinuclear nickel(II) complex $[\text{Ni}_2(\mu\text{-OH})_2(\text{tpa})_2](\text{ClO}_4)_2$ [tpa = tris-(2-pyridylmethyl)-amine] in solution forming a novel square-planar nickel(II) complex $\text{Ni}\{\text{HN}=\text{C}(\text{Me})\text{-N}=\text{C}(\text{Me})\text{-NH}\}_2$.

Acetonitrile is one of the common solvents that is widely used to study processes in solution. With most 3d-transition metal ions acetonitrile behaves as a relatively weak monodentate ligand, providing inorganic chemists with a perfect media for numerous reactions.¹ However, transition metal complexes are well known to catalyze and promote the reactions of nitriles, *e.g.* their reduction, redox coupling, hydrolysis, and addition of nucleophiles.^{2,3} In some cases nitrile, $\text{R}-\text{C}\equiv\text{N}$, adds to a ligand (L^- or LH) yielding a new composite ligand ($\text{L}-\text{C}(\text{R})=\text{N}^-$ or $\text{L}-\text{C}(\text{R})=\text{NH}$) within the coordination sphere of a metal ion.^{2,4} Here we report the first case of a reaction, in which acetonitrile undergoes self-condensation into an efficient bidentate ligand (*N*-acetimidoylacetylamine) under the action of a metal complex, $[\text{Ni}_2(\mu\text{-OH})_2(\text{tpa})_2](\text{ClO}_4)_2$ **1**.



Metal complexes with the tripodal tetramine ligand tpa and its homologs have been widely used in metalloenzyme modeling.^{5,6} In particular, complex **1** was found to be a good catalyst for transesterification and carbon dioxide hydration.^{7,8}

We prepared complex **1** by a simplified, one-pot procedure adapted from the original method proposed by Ito and Takita.⁷ Its identity was established by elemental analysis, mass spectrometry, and UV-VIS spectroscopy. Solid **1** gives a blue solution in acetonitrile. When stored in a tightly sealed container at room temperature, this solution very slowly (within months) turns dark-purple and precipitates an orange-yellow crystalline material. If the acetonitrile solution of **1** is kept at 75 °C, the transformation is completed in 2 days. Recrystallization from acetonitrile and drying under vacuum gives pure diamagnetic complex **2** with the formula $\text{Ni}(\text{C}_4\text{H}_8\text{N}_3)_2$.[†]

A single crystal X-ray diffraction study of solvated complex $\text{2}\cdot\text{2H}_2\text{O}$ revealed that tpa and hydroxide ligands around $\text{Ni}(\text{II})$ ions are lost and substituted by a new unexpected ligand, *N*-acetimidoylacetylamine (Fig. 1).[‡] Each $\text{Ni}(\text{II})$ ion is coordinated by two bidentate *N*-acetimidoylacetylaminato anions, forming

the mononuclear molecular complex **2**. A molecule of **2** contains two six-membered flat metalocycles (deviation of atoms from the mean plane <0.02 Å, and <0.05 Å, if methyl groups are taken into account). The Ni–N bond lengths (1.85 Å) are similar to other $\text{Ni}(\text{II})$ square planar low-spin complexes with imine nitrogen donor atoms.¹ In the crystal lattice of $\text{2}\cdot\text{2H}_2\text{O}$, individual molecules of **2** are connected *via* hydrogen bonding with water molecules (Fig. 1; Table S1[†]).

A mass spectrometry study showed that *N*-acetimidoylacetylamine originated from the solvent (acetonitrile). The crude reaction solution after heating complex **1** in acetonitrile shows signals at m/z 255, 291, 347, 407 and 447, which can be ascribed to the molecular ions of 2^+ , $[\text{tpaH}]^+$, $[\text{Ni}(\text{tpa})]^+$, $[\text{Ni}(\text{tpa})(\text{MeCO}_2)]^+$ and $[\text{Ni}(\text{tpa})(\text{ClO}_4)]^+$, respectively, according to their positions and the relative intensities of isotope satellites. When the reaction is carried out with CD_3CN instead of regular acetonitrile, the peaks of 2^+ and $[\text{Ni}(\text{tpa})(\text{MeCO}_2)]^+$ are shifted 12 and 3 daltons up, respectively. Therefore, the source of the four methyl groups in the molecule of **2** is acetonitrile. There is a concomitant formation of acetate from acetonitrile. The tpa ligand remains intact in the course of the reaction and is partially released in the free form. The stoichiometry of the overall transformation can be tentatively expressed by eqn. (1)



The role of **1** as a nickel complex promoting the acetonitrile transformation is specific. In separate experiments under similar conditions, no reaction with acetonitrile was observed, if complex **1** was substituted by $\text{NiX}_2\cdot 6\text{H}_2\text{O}$ ($\text{X} = \text{Cl}, \text{ClO}_4, \text{NO}_3$), $\text{Ni}(\text{MeCO}_2)_2\cdot 4\text{H}_2\text{O}$, $\text{Ni}(\text{ClO}_4)_2\cdot 6\text{H}_2\text{O} + \text{py}$ (1:4), or $\text{Ni}(\text{ClO}_4)_2\cdot 6\text{H}_2\text{O} + \text{tpa}$ (1:1).

There are only scarce reports of metal complexes with protonated *N*-acetimidoylacetylamine ligand

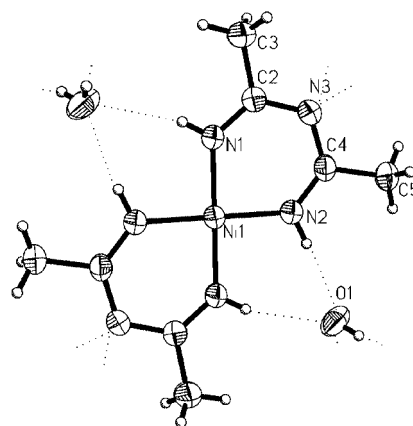


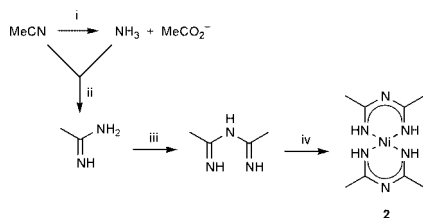
Fig. 1 ORTEP drawing of $\text{2}\cdot\text{2H}_2\text{O}$. Selected bond lengths (Å) and angles (°): Ni–N2 1.850(2), Ni–N1 1.851(2), N1–C2 1.296(3); C2–N3 1.360(3), N3–C4 1.353(3); C4–N2 1.296(3), N1–Ni–N2 89.31(8).

† Electronic supplementary information (ESI) available: Table S1: hydrogen bonds in the crystal structure of complex $\text{2}\cdot\text{2H}_2\text{O}$. See <http://www.rsc.org/suppdata/cc/b1/b101893k/>

‡ Dedicated to Professor Konstantin B. Yatsimirskii on the occasion of his 85th birthday.

[HN{C(Me)=NH}₂, HL]. Two copper(II) complexes (CuCl₂·*n*HL, *n* = 1, 2) have been prepared, but not characterized in detail.⁹ The only compound characterized by X-ray diffraction is a protonated form of complex **2**, namely green 2·1.5HCl·3H₂O, formed upon self-condensation of acetamidine [MeC(=NH)NH₂] and NiCl₂·6H₂O in methanolic solution.¹⁰ The structures of both complexes with square-planar Ni(II) centers are very similar. The C–N bond lengths in **2** are more uniform than in the protonated complex in agreement with more ‘aromatic’ character of the chelate metalocycle. Complex **2** seems to be the first molecular *N*-acetimidoylacetylacetaminate metal complex prepared to date. This is in contrast to the chemistry of metal acetylacetonates, which have been extensively studied and found numerous practical applications.¹ *N*-Acetimidoylacetylacetaminate is isoelectronic with acetylacetonate, but has a significantly stronger ligand field. As a result, **2** and 2·2H₂O have low-spin square-planar Ni(II) ions, while [Ni₃(acac)₆] and [Ni(acac)₂(H₂O)₂] are high-spin pseudo-octahedral Ni(II) complexes with bridging acac ligands and coordinated water molecules, respectively.^{1,11}

Based upon known literature precedence, we can propose a sequence of events resulting in the overall transformation of acetonitrile into the acetimidoylacetylacetaminate complex and acetate (Scheme 1).



Scheme 1 Tentative mechanism of formation of complex **2** from acetonitrile and complex **1** (see text for the explanation of steps).

(i) Acetonitrile reacts with the hydroxide ligands of complex **1** or with trace water forming acetamide and, subsequently, acetate and ammonia. Catalytic activity of transition metal complexes in the hydrolysis of nitriles is well documented.² On the other hand, complex **1** is known to be a potent catalyst of transesterification.⁸

(ii) Acetonitrile and NH₃ yield acetimidine. This reaction is also known to be catalyzed by metal ions.¹²

(iii) *N*-Acetylacetimidine is formed upon condensation of an acetimidine molecule with acetonitrile, acetamide, or another acetimidine molecule. Templated condensation of acetimidine in the presence of NiCl₂·6H₂O in methanolic solution to form 2·1.5HCl·3H₂O has been reported.¹⁰

(iv) *N*-Acetylacetimidine, which is isoelectronic with acetylacetonate, but apparently has a much stronger ligand field, can act as a good new ligand for Ni(II). The net result of the reaction is the total displacement of the old ligands in complex **1**, including the tetradentate tpa, and the formation of a new complex Ni{HN=C(Me)–N=C(Me)–NH}₂ **2**.

Some other precedence for the reaction exists. Coupling of alkyl nitriles into 3,5-dialkyl-1,2,4-triazoles promoted by a dicopper complex has been reported.³ Oligomerization of CF₃CN and CCl₃CN in the presence of transition metal complexes leads to the formation of the corresponding halogenated *N*-acetimidoylacetylacetamides, but acetonitrile is unreactive under the same conditions.^{13,14} To the best of our knowledge, the transformation of a non-halogenated nitrile into an *N*-imidoylamidine promoted by a metal complex has not been observed before.

The behavior of dinickel(II) complex **1** can be contrasted to its diiron(III) analog, [Fe₂(μ-O)(tpa)₂(OH)(H₂O)]³⁺, which reacts with MeCN to form a complex with a bridging acetamide ligand [Fe₂(μ-O){μ-OC(Me)NH}(tpa)₂]³⁺.⁵ In that case, the transformation of acetonitrile stops on acetamide, probably because the amidate [Fe₂^{III}(μ-O)(μ-OC(R)NH)(tpa)₂]³⁺ complexes are coordinatively saturated and stable towards hydrolysis or dissociation.¹⁵ In an additional experiment we found that

complex **1** does not bind acetamide in solution as its diferric analog does.

In conclusion, we have demonstrated that a dinuclear hydroxo-bridged nickel(II) complex promotes self-condensation of acetonitrile into *N*-acetimidoylacetylacetamide, which acts as an efficient acetylacetonate-like bidentate ligand, displacing the old ligands around Ni(II) and forming a new molecular homoleptic bis(*N*-acetimidoylacetylacetaminate)nickel(II) complex. This reaction shows that possible side-reactions should always be considered in studies involving metal complexes and acetonitrile.

Notes and references

§ *Synthesis of 1*. Ni(ClO₄)₂·6H₂O (0.366 g, 1 mmol) and tpa (0.29 g, 1 mmol) were dissolved in 10 ml of water on stirring. To the resulting purple solution was added 1 ml of 1 M NaOH solution. The light-blue precipitate of crude complex **1** was left overnight for ripening, filtered off, washed with ice water, and dried under vacuum. Its recrystallization from acetonitrile-diethyl ether under N₂ gave pure **1** as dark-blue crystals. Yield: 0.37 g (80%). Calc. for C₃₆H₃₈Cl₂N₈Ni₂O₁₀: C, 46.44; H, 4.11; N, 12.04. Found: C, 46.47; H, 3.98; N, 11.92%; (ESMS⁺, MeCN): *m/z* 833 ([Ni₂(OH)₂(tpa)₂(ClO₄)⁺, 5%), 447 ([Ni(tpa)(ClO₄)⁺, 95%), 383 ([Ni(tpa)(H₂O)(OH)]⁺, 100%); UV–VIS: λ_{max}/nm (ε/M⁻¹ cm⁻¹ per Ni₂): MeOH: 589 (28), 795 (sh) (18), 980 (46); MeCN: 588 (40), 790 (sh) (12), 980 (34).

¶ *Synthesis and properties of 2*: complex **1** (0.37 g; 0.4 mmol) and 3.7 ml of acetonitrile are placed into a vial, tightly closed, and heated for 2 days at 75 °C. The resulting dark-purple solution is cooled forming orange–yellow crystalline material (2·2H₂O as suggested by a single crystal X-ray diffraction study). Its recrystallization from hot acetonitrile and drying under vacuum gives pure complex **2**. Yield: 0.031 g (15% based on Ni). Calc. for C₈H₁₆N₆Ni: C, 37.69; H, 6.33; N, 32.96. Found: C, 37.58; H, 6.39; N, 32.81%; ESMS (MeCN): *m/z* +255 (2H⁺, 100%); –253 (2–H, 100%); NMR (25 °C, D₆-DMSO): ¹H, δ 6.20 (s, 4H, NH), 1.795 (s, 12H, Me); ¹³C, δ 164.5, 26.2; UV–VIS (DMSO): λ_{max}/nm (ε/mM⁻¹ cm⁻¹): 290 (sh) (3.0), 321 (1.9), 336 (1.7), 465 (0.040); FT-IR (KBr): ν/cm⁻¹: 3280 (νNH), 2960 (ν_{as}Me), 2850 (ν_sMe), 1580 (ν_{as}CN), 1470, 1420, 1378, 1190, 946, 665, 516.

|| *Crystal data for 2·2H₂O*: C₈H₂₀N₆NiO₂, *M_w* = 291.01, orthorhombic, space group *Pbca* (no. 61), *a* = 13.040(3), *b* = 14.150(3), *c* = 7.4400(10) Å, *V* = 1372.8(5) Å³, *Z* = 4, μ(Mo–Kα) = 1.415, *T* = 293(2) K, 1823 reflections measured, ψ-scan absorption correction, *R*₁[*I* > 2σ(*I*)] = 0.032, *wR*₂ = 0.098 for all reflections. The structure was solved by direct methods using SHELXS-97 and refined with all data by full-matrix least squares on *F*² using SHELXL-97. All non-hydrogen atoms were refined anisotropically and hydrogen atoms were refined as isotropic. CCDC 162662. See <http://www.rsc.org/suppdata/cc/b1/b101893k/> for crystallographic data in CIF or other electronic format.

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