

Conversion of alkanenitriles to amidines and carboxylic acids mediated by a cobalt(II)–ketoxime system

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The conversion of sterically unhindered organonitriles RCN (R = Me, Et, *n*-Pr, *n*-Bu) into the corresponding amidines RC(=NH)NH₂, isolated as the nitrate salts, and carboxylic acids RCO₂H proceeds in the appropriate nitrile as solvent in the presence of Co(NO₃)₂·6H₂O or the cobalt(II) complex *trans*-[Co(MeCN)₂(H₂O)₄](NO₃)₂ and a ketoxime R'₂C=NOH (R' = Me₂ or C₅H₁₀) but does not proceed at all with either the cobalt compound or the ketoxime taken alone. The amidinium nitrates were characterized by C, H, N elemental analyses, FAB⁺-MS, IR, ¹H and ¹³C{¹H} NMR spectroscopies and the structures of RC(=NH₂)NH₂⁺NO₃⁻ (R = Et, *n*-Pr, *n*-Bu) were determined by X-ray crystallography, while the carboxylic acids were identified by GC and ¹H and ¹³C{¹H} NMR spectroscopies. The reaction proceeds differently with sterically hindered organonitriles, e.g. *i*-PrCN and *t*-BuCN, and—instead of amidinium salts—ammonium nitrate and the appropriate carboxylic acids were identified. The structure of *trans*-[Co(MeCN)₂(H₂O)₄](NO₃)₂, which is anticipated to be an intermediate in the reaction of Co(NO₃)₂·6H₂O, was determined by X-ray diffractometry.

Introduction

It is well-known that the development of efficient methods for the formation of the C–N amide linkage is of paramount importance due to the high synthetic utility of amides, their numerous industrial applications and their pharmacological significance.^{1,2} As far as amidines RC(=NH)NR'R'' are concerned, their *direct* synthesis from RCN and R'R''NH can only be achieved when the nitrile bears a strong electron-acceptor group R, e.g. CCl₃.³ A general, although more time-consuming, method for preparation of amidines is based on the Pinner reaction and involves the reaction between RCN and R'OH (or R'SH, the so-called Thio-Pinner reaction^{2,4}) in a non-aqueous solvent containing substantial amounts of HX (X = Cl, Br) followed by the interaction of the imino ester salt RC(OR')=NH·HX thus formed with ammonia, primary or secondary amines.^{1,5,6} It was also established that unactivated organonitriles RCN, *i.e.* with electron-donor groups, can still be activated towards the coupling with amines by application of Lewis acids such as FeCl₃, AlCl₃, ZnCl₂⁷ or MeAl(Cl)NR'R''.^{8–10}

Other metal-based systems, e.g. Ln(SO₃CF₃)₃ (Ln = lanthanide)^{11,12} or CuCl,¹³ have also proved to be useful in the generation of amidines from nitriles and primary or secondary amines. In fact, lanthanide(III) triflates catalyze the reaction of nitriles (NCR) with primary amines (R'NH₂) and diamines [H₂N(CH₂)_{*n*}NH₂, *n* = 2–4] to form *N,N'*-disubstituted amidines RC(=NR')NHR' (R = Me, Et, Ph; R' = alkyl, Ph) and cyclic amines, respectively, with loss of NH₃.¹² More recently a facile synthesis of amidines involving the intermolecular reductive coupling of nitriles with organic nitro or aza compounds induced by SmI₂,¹⁴ TiCl₄/Sm^{15,16} or TiCl₄/Zn¹⁶ has been reported.

As an extension of our previous work on platinum-,^{17,18} rhodium-¹⁹ and rhenium-mediated²⁰ organonitrile–oxime

couplings giving iminoacylated oximes^{17–20} or Δ⁴-1,2,4-oxadiazolines¹⁸ we have focused our attention on 3d metals and attempted to promote the nitrile–oxime coupling using the cobalt(II) ion. In contrast to our expectations, we observed, instead of the iminoacylation reaction, an intriguing conversion of an alkanenitrile to amidine and carboxylic acid and these results are reported herein.

Results and discussion

We recently reported an unusual metal-mediated coupling between nitriles bound to a metal center and oximes HON=CR'₂ which gave addition products with either monodentate [M]–HN=C(R)ON=CR'₂ [M = Pt(IV),¹⁷ Re(IV)²⁰] or bidentate [M]–NH=C(R)–O–N=CR'₂ [M = Rh(III)¹⁹] iminoacylated ligands depending on the metal center. Being interested in extending our research into nitrile–oxime couplings to other metal systems we investigated the reactions with 3d metals and, in particular, we studied nitrile and oxime reactions mediated by the cobalt(II) ion. In the latter case, however, the reaction took a different route and we observed, instead of the iminoacylation, the facile conversion of an alkanenitrile, RCN, to the appropriate amidine, RC(=NH)NH₂, and carboxylic acid, RC(=O)OH. The amidines were isolated in a good yield as their nitrate salts.

Isolation and identification of amidinium salts

The conversion of RCN (R = Me, Et, *n*-Pr, *n*-Bu) proceeds at 50 °C for 8 h in the appropriate nitrile as solvent in the presence of Co(NO₃)₂·6H₂O and a ketoxime R'₂C=NOH (R' = Me₂ or C₅H₁₀), but does not proceed at all with either the cobalt salt or the ketoxime taken alone. With a view to achieving better reaction conditions, separation of amidinium salts and yield

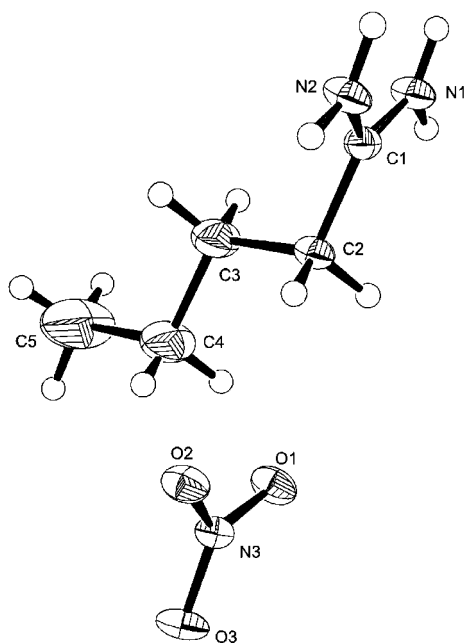


Fig. 1 ORTEP view of the molecular structure of $n\text{-BuC}(\text{NH}_2)_2^+\text{NO}_3^-$ with the atom-numbering shown. The thermal ellipsoids are drawn at the 50% probability level.

optimisation, the effect of stoichiometric $\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ –ketoxime ratios ranging from 1 : 1 to 1 : 6 were investigated. The best results were obtained with a molar ratio 1 : 4; with less oxime, e.g. 1 : 2, the rate of reaction decreases significantly and it takes *ca.* 24 h to complete the reaction. The conversion can also be completed in *ca.* 1 h upon reflux but isolated products in these cases are slightly beige and—although we were unable to detect any impurities by routine methods—the products should be recrystallised.

In all four cases ($\text{R} = \text{Me}, \text{Et}, n\text{-Pr}, n\text{-Bu}$), the amidines were released and isolated from the reaction mixture as the amidinium nitrate salts $[\text{RC}(\text{=NH}_2)\text{NH}_2]^+(\text{NO}_3)^-$. These compounds were characterized: (i) by C,H,N elemental analyses, FAB⁺-MS, IR, ¹H and ¹³C{¹H} NMR spectroscopies; (ii) by comparison of the obtained crystal lattice parameters and the melting point for acetamidinium nitrate, $\text{MeC}(\text{=NH}_2)\text{NH}_2^+\text{NO}_3^-$, with those known in the literature;²¹ (iii) by comparison of ¹³C{¹H} NMR spectra of $\text{MeC}(\text{=NH}_2)\text{NH}_2^+\text{NO}_3^-$ from this work and that of commercially available (Lancaster) $\text{MeC}(\text{=NH}_2)\text{NH}_2^+\text{Cl}^-$ which showed substantial similarities despite different counterions; (iv) by X-ray crystallographic studies of $\text{RC}(\text{NH}_2)_2^+\text{NO}_3^-$ ($\text{R} = \text{Et}, n\text{-Pr}, n\text{-Bu}$) (see Fig. 1 for $n\text{-BuC}(\text{NH}_2)_2^+\text{NO}_3^-$) which gave very similar results for the $\text{C}(\text{NH}_2)_2$ moieties and also good agreement with bond lengths and angles of the previously reported²¹ acetamidinium nitrate.

All amidinium nitrate salts form stacked double-layer structures. The non-polar alkyl ends of the molecules are oriented towards each other forming a non-polar “inner-layer” (Fig. 2). Only weak van der Waals interactions occur between the alkyl chains. The shortest C···C distance of 3.83 Å is found in $n\text{-PrC}(\text{NH}_2)_2^+\text{NO}_3^-$ (2). The $-\text{NH}_2$ ends of the cation and the NO_3^- counteranions form a polar “outer layer”, which is further stabilized by hydrogen bonds. The shortest $\text{NH}\cdots\text{O}$ distances within the polar layer are *ca.* 2.92 Å, whereas the shortest $\text{NH}\cdots\text{O}$ distance between the neighbouring polar layers is over 3.1 Å with the $\text{N}-\text{H}\cdots\text{O}$ angles typically less than 120° indicating only weak interactions.

The reaction proceeds differently with sterically hindered organonitriles, e.g. *i*-PrCN and *t*-BuCN. In these cases we were unable to isolate amidinium salts but, instead, obtained NH_4NO_3 [identified by its IR spectrum, melting point and elemental (N and H) analyses] and the appropriate carboxylic acids (identified by ¹H NMR spectroscopy).

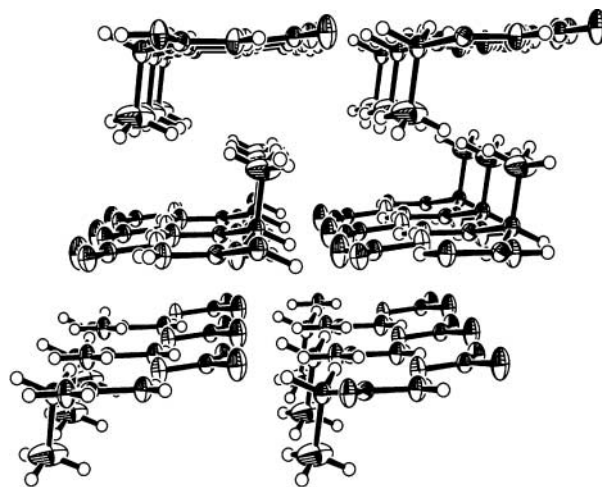


Fig. 2 Packing diagram of $\text{EtC}(\text{NH}_2)_2^+\text{NO}_3^-$.

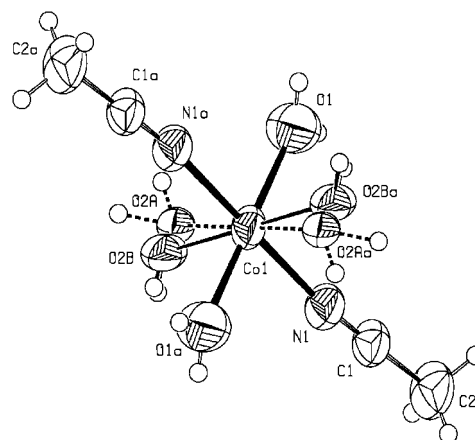


Fig. 3 ORTEP view of the molecular structure of the complex cation with the atom-numbering shown. The thermal ellipsoids are drawn at the 50% probability level. The O(2) disorder of the water ligand is also shown with site occupation factors of 0.43 for O(2)A and 0.57 for O(2)B.

Isolation and identification of other products from the reaction

Slow evaporation of the filtrate after the reaction, in NCME, allowed the isolation of hygroscopic pink crystals of *trans*- $[\text{Co}(\text{MeCN})_2(\text{H}_2\text{O})_4](\text{NO}_3)_2$. It should be pointed out that, as has been demonstrated in a separate experiment, this cobalt–solvento complex in the presence of propan-2-one oxime promotes the conversion of nitriles similarly to $\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$. The structure of *trans*- $[\text{Co}(\text{MeCN})_2(\text{H}_2\text{O})_4](\text{NO}_3)_2$ was determined by X-ray single-crystal diffractometry (Fig. 3).

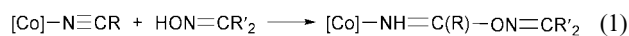
In this complex, the coordination polyhedron is a slightly distorted octahedron formed by four oxygen and two nitrogen atoms. The Co atom was located in a special position (0.5,0,0.5) with only half of the molecule being found in the asymmetric unit. A disordered model was used to refine the O(2) water molecule; it was assumed that two alternative conformations were possible with site occupation factors of the two molecules adding up to unity. The Co–O [2.069–2.09 Å] and Co–N [2.120(4) Å] bond lengths and also all bond angles around the Co centre agree well with the mean reported values.²² The bond lengths and angles in the nitrile linkage are also typical of normal values.²³ The X-ray analysis of the related bromide salt of the cobalt complex has recently been reported,²⁴ showing similar crystallographic data.

Three other products were also isolated. The first one is ammonium nitrate found as an admixture (crystals of different shape were separated mechanically from the crystals of the amidinium salts) in the reaction with sterically unhindered nitriles and as a regular product in the reactions involving

i-PrCN and *t*-BuCN (see above). The second one is a carboxylic acid which was detected by both gas chromatography and ^1H and $^{13}\text{C}\{^1\text{H}\}$ NMR spectroscopy after acidification of the filtrate with HCl followed by extraction of RCO_2H in chloroform. The third product is formed as a purple powder in the synthesis of acetamidine when the oxime– $\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ ratio is less than 1 : 1. Although we were unable to identify this Co-containing material (see Experimental section), its acidification with aqueous HNO_3 followed by extraction of the products in chloroform and subsequent GC and ^1H and $^{13}\text{C}\{^1\text{H}\}$ NMR analyses allowed the identification of acetic acid.

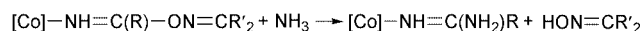
Final remarks

Isolation and identification of the products of these reactions has allowed us to suggest a plausible mechanism. We assume that, in the initial stage, $\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ is converted to the solvento complex *trans*- $[\text{Co}(\text{MeCN})_2(\text{H}_2\text{O})_4](\text{NO}_3)_2$ in acetonitrile solution or, when using a different organonitrile, to a related nitrile complex. Ligation of RCN to the metal centre activates it towards nucleophilic attack by both H_2O^{25} (giving ammonia and carboxylic acid; a similar two-step metal-mediated hydrolysis is known²⁶) and $\text{R}'_2\text{C}=\text{NOH}$,^{17,19,20} [eqn. (1)].



A secondary reaction between ammonia [see eqn. (2)]

(2)



or ammonium ion and $[\text{Co}]-\text{NH}=\text{C}(\text{R})-\text{ON}=\text{CR}'_2$ furnishes amidine and liberates the oxime; this process is similar to the second step of the Pinner reaction,²⁷ *i.e.* formation of amidines upon interaction of amines with imino esters $\text{NH}=\text{C}(\text{R})\text{OR}'$.

Although, for reasons of simplicity, eqn. (2) is illustrated with the use of free ammonia, the mechanism of this stage remains unclear and we cannot rule out intramolecular coupling. Indeed, addition of NH_3 or NH_4NO_3 to the reaction mixture led, in the former case, to the darkening and deterioration of the mixture, while the latter had no effect on the process.

Eventually the amidine complex [eqn. (2)] liberates the amidine ligand in the protonated amidinium form upon reaction (which may be assisted by solvolysis) with carboxylic acid (formed by nitrile hydrolysis as indicated above). It is unclear if the carboxylate ion thus obtained would remain free or bind to the metal centre (the latter case would account for the non-catalytic character of the process) being liberated at a later stage on acidification with HCl. Taking into account the possibility of two concurrent nucleophilic additions to a cobalt-bound nitrile one might understand why the steric properties of the substituent R in RCN play a dramatic role in the overall reaction. Indeed, the addition of the rather bulky ketoxime should be hampered by bulky organonitriles making favourable the addition of water. Moreover, our preliminary results²⁸ indicate that the electronic properties of the substituent R also play a significant role forwarding the process in one or another direction depending on its donor–acceptor character. Thus, electron-acceptor groups R, *e.g.* ClCH_2 , Ph or *p*- $\text{MeOC}_6\text{H}_4\text{CH}_2$, make addition of water so favorable that only the formation of carboxamides was observed but this study is still in progress and will be reported separately.

The one-step formation of amidines starting from nitriles bearing an electron-donor group might represent a viable route to amidines especially if catalytic conditions can be discovered. To achieve this we plan to study the reaction of cobalt salts in various oxidation states with different anions,

and also to attempt the reaction with other 3d metal ions, including “green” iron systems; this work is underway in our group.

Experimental

Materials and instruments

Cobalt(II) hexaaquanitrate (Merck), acetonitrile (Lab-Scan), propionitrile (Aldrich), butyronitrile (Aldrich), valeronitrile (Aldrich), propan-2-one oxime (Lancaster) and cyclohexanone oxime (Aldrich) were obtained from commercial sources and used as received. C,H,N elemental analysis was carried out by the Microanalytical Service of the Instituto Superior Técnico. Melting points were determined on a Kofler hot stage apparatus. Positive-ion FAB mass spectra were obtained on a Trio 2000 instrument by bombarding 3-nitrobenzyl alcohol (NBA) matrices of the samples with 8 keV (*ca.* 1.18×10^{15} J) Xe atoms. Mass calibration for data system acquisition was achieved using CsI. Infrared spectra ($4000\text{--}400\text{ cm}^{-1}$) were recorded on a BIO-RAD FTS 3000MX instrument in KBr pellets (*m-w* = medium–weak). ^1H and $^{13}\text{C}\{^1\text{H}\}$ NMR spectra were measured on a Varian UNITY 300 spectrometer at ambient temperature. GC was performed using a FISOONS Instruments GC 8000 series gas chromatograph with DB WAX fused silica capillary column (P/N 123–7032) and the JASCO-BORWIN v.1.50 software.

X-Ray crystallography †

Colourless crystals of $\text{EtC}(\text{NH}_2)_2^+\text{NO}_3^-$ (**1**), $n\text{-PrC}(\text{NH}_2)_2^+\text{NO}_3^-$ (**2**) and $n\text{-BuC}(\text{NH}_2)_2^+\text{NO}_3^-$ (**3**) were obtained by recrystallization from acetone, acetonitrile and a mixture of acetone and methanol, respectively. Pink crystals of *trans*- $[\text{Co}(\text{MeCN})_2(\text{H}_2\text{O})_4](\text{NO}_3)_2$ (**4**) were grown by slow evaporation of the mother liquor after filtration from $[\text{MeC}(\text{=NH}_2)\text{-NH}_2](\text{NO}_3)$. X-Ray diffraction data were collected with a Nonius-Kappa CCD diffractometer (complexes **1–3**) or an Enraf-Nonius CAD4 diffractometer (structure **4**), equipped with graphite monochromator and using Mo-K α radiation. DENZO and SCALEPACK²⁹ programs were used for cell refinements and data reduction for **1–3**. Structures were solved by direct methods by SIR92³⁰ or SIR97³¹ programs with the WinGX³² graphical user interface or by SHELXS-86 program.³³ The structure refinements were carried out with SHELXL-97.³⁴ In structures **1–3** hydrogens bonded to the nitrogens were located from the difference Fourier map and refined isotropically. In **4** one of the water ligands was disordered in two positions which were refined with equal anisotropic displacement parameters. The water hydrogens in **4** were located from a difference Fourier map and refined by using fixed O–H bond length of 0.82 Å and equal isotropic displacement parameters. All other hydrogens were constrained to ride on their parent atom. Crystallographic data are summarized in Table 1 and selected bond lengths and angles in Tables 2 and 3. The molecular structure of $n\text{-BuC}(\text{NH}_2)_2^+\text{NO}_3^-$ and the numbering scheme of the molecules $\text{EtC}(\text{NH}_2)_2^+\text{NO}_3^-$, $n\text{-PrC}(\text{NH}_2)_2^+\text{NO}_3^-$ and $n\text{-BuC}(\text{NH}_2)_2^+\text{NO}_3^-$ are shown in Fig. 1. A packing diagram of $\text{EtC}(\text{NH}_2)_2^+\text{NO}_3^-$ is shown in Fig. 2 and the molecular structure of *trans*- $[\text{Co}(\text{MeCN})_2(\text{H}_2\text{O})_4](\text{NO}_3)_2$ in Fig. 3.

Synthetic work and characterisation

General procedure. $\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ (219 mg, 1 mmol) is dissolved in the corresponding nitrile (5 ml), whereafter a ketoxime, *i.e.* $\text{Me}_2\text{C}=\text{NOH}$ or $(\text{C}_5\text{H}_{10})\text{C}=\text{NOH}$ (4 mmol) is

† CCDC reference number(s) 158060–158063. See <http://www.rsc.org/suppdata/p1/b1/b101337h/> for crystallographic files in cif. or other electronic format.

Table 1 Crystallographic data for EtC(NH₂)₂⁺NO₃⁻, *n*-PrC(NH₂)₂⁺NO₃⁻, *n*-BuC(NH₂)₂⁺NO₃⁻ and *trans*-[Co(MeCN)₂(H₂O)₄](NO₃)₂

Empirical formula	EtC(NH ₂) ₂ ⁺ NO ₃ ⁻	<i>n</i> -PrC(NH ₂) ₂ ⁺ NO ₃ ⁻	<i>n</i> -BuC(NH ₂) ₂ ⁺ NO ₃ ⁻	C ₄ H ₆ CoN ₂ O ₄ ·2(NO ₃)
<i>M</i>	135.13	149.16	163.18	337.12
Temp./K	120	120	120	293
$\lambda/\text{\AA}$	0.71073	0.71073	0.71073	0.71073
Crystal system	Triclinic	Monoclinic	Triclinic	Monoclinic
Space group	<i>P</i> $\bar{1}$ (No. 2)	<i>P</i> 2 ₁ / <i>n</i> (No. 14)	<i>P</i> $\bar{1}$ (No. 2)	<i>P</i> 2 ₁ / <i>c</i> (No. 14)
<i>a</i> /\AA	6.5627(2)	6.4444(4)	6.4391(2)	7.8179(10)
<i>b</i> /\AA	6.6924(2)	17.5130(15)	6.7648(2)	12.7715(8)
<i>c</i> /\AA	8.2274(3)	6.8157(5)	10.527(4)	7.9825(6)
<i>a</i> /deg	72.830(2)	90	73.655(2)	90
β /deg	87.467(2)	98.265(5)	81.477(2)	117.723(9)
γ /deg	82.367(2)	90	82.105(2)	90
<i>V</i> /\AA ³	342.181(19)	761.24(10)	432.95(17)	705.53(11)
<i>Z</i>	2	4	2	2
$\rho_{\text{calc}}/\text{g cm}^{-3}$	1.312	1.301	1.252	1.587
$\mu(\text{Mo-K}\alpha)/\text{mm}^{-1}$	0.115	0.110	0.103	1.267
Reflections collected	2183	1944	2669	1640
Independent reflections	1240	1273	1572	1533
Reflections observed	1165	1117	1465	1047
<i>R</i> _{int}	0.0127	0.0311	0.0134	0.023
<i>R</i> ₁	0.0338	0.0557	0.0370	0.0459
<i>wR</i> ₂ ^a	0.0873	0.1442	0.0934	0.1044

^a $w = 1/[\sigma^2 \times F_o^2 + (0.0675 \times P)^2 + 0.3100 \times P]$, where $P = [\max(F_o, 0)^2 + 2 \times F_c^2]/3$.

Table 2 Selected bond lengths (\AA) and angles (°) for EtC(NH₂)₂⁺NO₃⁻, *n*-PrC(NH₂)₂⁺NO₃⁻ and *n*-BuC(NH₂)₂⁺NO₃⁻

	EtC(NH ₂) ₂ ⁺ NO ₃ ⁻	<i>n</i> -PrC(NH ₂) ₂ ⁺ NO ₃ ⁻	<i>n</i> -BuC(NH ₂) ₂ ⁺ NO ₃ ⁻
N(1)–C(1)	1.3093(16)	1.310(3)	1.3126(16)
N(2)–C(1)	1.3068(15)	1.302(3)	1.3099(16)
C(1)–C(2)	1.5002(15)	1.500(3)	1.4984(16)
C(2)–C(3)	1.5149(19)	1.540(4)	1.525(2)
C(3)–C(4)		1.502(4)	1.525(2)
C(4)–C(5)			1.521(3)
N(2)–C(1)–N(1)	121.30(11)	121.8(2)	121.43(11)

Table 3 Bond lengths (\AA) and angles (°) for *trans*-[Co(MeCN)₂(H₂O)₄](NO₃)₂

Co1–O1	2.072(4)	N1–C1	1.122(5)
Co1–O2A	2.063(14)	C1–C2	1.456(7)
Co1–O2B	2.08(2)	O3–N2	1.238(6)
Co1–N1	2.120(3)	O5–N2	1.204(6)
		O4–N2	1.242(5)
O1–Co1–O2A	83.5(4)	N1–C1–C2	179.6(5)
O1–Co1–O2B	98.7(6)	O3–N2–O4	118.2(4)
O1–Co1–N1	91.46(14)	O3–N2–O5	119.6(4)
O2B–Co1–N1	91.9(7)	O4–N2–O5	122.2(4)
O2A–Co1–N1	87.7(4)		
Co1–N1–C1	172.6(3)		

added. The mixture is stirred at 50 °C for 8 h (if the quantity of the oxime was decreased two-fold the rate of reaction decreases significantly and it takes *ca.* 24 h to complete the reaction). In all cases the colour of the reaction mixture changes in time from violet–pink to brown and colourless crystals of the corresponding amidinium nitrate salts are formed, they are filtered off, washed with three 5 ml portions of acetone and dried *in vacuo* at room temperature. Slow evaporation of the filtrate gives pink very hygroscopic crystals of *trans*-[Co(MeCN)₂(H₂O)₄](NO₃)₂. In the reaction of *i*-PrCN and *t*-BuCN with Co(NO₃)₂·6H₂O–propan-2-one oxime performed under the same conditions, NH₄NO₃ was formed as the main product and no amidine was detected. Identification of NH₄NO₃ was based on the elemental analysis (N,H), melting point and IR spectrum. NH₄NO₃ was also isolated—but only as a by-product in minor quantities—in some cases from a reaction mixture containing EtCN and *n*-PrCN. Carboxylic acids formed in the course of the reaction were identified by both GC and ¹H and ¹³C{¹H} NMR spectroscopy.

The purple powder formed in the synthesis of acetamidine

when the oxime–Co(NO₃)₂·6H₂O ratio is less than 1 : 1 has the following analytical data. Anal. Found: C, 20.05; H, 5.31; N, 25.47. FAB⁺-MS, *m/z*: 212. IR spectrum (KBr), selected bands, cm⁻¹: 3339 s, 2811 s, 1703 s, 1402 s, 1119 s, 1047 s, 823 s, 700 s, 527 s, 446 s.

MeC(=NH₂)NH₂⁺NO₃⁻. Identical samples were obtained from the reaction with involvement of either Co(NO₃)₂·6H₂O–propan-2-one oxime, Co(NO₃)₂·6H₂O–cyclohexanone oxime or *trans*-[Co(MeCN)₂(H₂O)₄](NO₃)₂–propan-2-one oxime systems. Yield is 65–75% based on Co. Anal. Calcd for C₂H₇N₃O₃: C, 19.84; H, 5.83; N, 34.70. Found: C, 19.52; H, 5.82; N, 34.75. FAB⁺-MS, *m/z*: 59 [M_{cation}]⁺. Mp = 195 °C [*lit.*²¹: 195 °C]. IR spectrum (KBr), selected bands, cm⁻¹: 3382 s ν (N–H), 1696 s and 1657 m–w ν (C=N) + δ (NH₂), 1384 s δ (NO₃), 1330 m–w δ (CH₃), 825 s ν (NO₃), 687 br,m δ (NH₂). ¹H NMR in D₂O, δ : 2.03 (s, 3H, Me), 7.87 (s, 2H, NH₂), 8.24 (s, 2H, NH₂). ¹³C{¹H} NMR in D₂O, δ : 17.9 (CH₃), 168.5 (C=N). Obtained crystal lattice parameters of the amidinium nitrate after its recrystallisation from MeCN: monoclinic, *P*2₁/*m*, *a* = 6.478, *b* = 6.427, *c* = 6.844 \AA, β = 97.69°, *V* = 282.17 \AA³ [*lit.*²¹ *P*2₁/*m*, *a* = 6.457, *b* = 6.442, *c* = 6.884 \AA, β = 97.56°, *V* = 283.91 \AA³].

EtC(=NH₂)NH₂⁺NO₃⁻. Yield is 63% based on Co. Anal. Calcd for C₃H₉N₃O₃: C, 26.66; H, 6.71; N, 31.09. Found: C, 26.74; H, 6.74; N, 30.88. FAB⁺-MS, *m/z*: 73 [M_{cation}]⁺, 145 [2M_{cation} – 2H]⁺, 208 [2M_{cation}]⁺NO₃⁻. mp = 193 °C. IR spectrum in KBr, selected bands, cm⁻¹: 3326 s, 3136 s ν (N–H), 1689 s ν (C=N) + δ (NH₂), 1383 s δ (NO₃), 824 m–w ν (NO₃), 705 br,m δ (NH₂). ¹H NMR in D₂O, δ : 1.07 (t, *J* 7.7 Hz, 3H, Me), 2.32 (q, *J* 7.7 Hz, 2H, CH₂). ¹³C{¹H} NMR in D₂O, δ : 10.2 (CH₃), 25.8 (CH₂); the solubility of EtC(=NH₂)–NH₂⁺NO₃⁻ is insufficient to observe the signal from C=N.

n-PrC(=NH₂)NH₂⁺NO₃⁻. Yield is 77% based on Co. Anal. Calcd for C₄H₁₁N₃O₃: C, 32.21; H, 7.43; N, 28.17. Found: C, 32.30; H, 7.86; N, 27.84. FAB⁺-MS, *m/z*: 87 [M_{cation}]⁺, 173

$[2M_{\text{cation}} - 2H]^+$, 236 $[2M_{\text{cation}}]NO_3^+$. Mp = 196 °C. IR spectrum (KBr), selected bands, cm^{-1} : 3335 s and 3139 s $\nu(N-H)$, 1695 s $\nu(C=N) + \delta(NH_2)$, 1384 s $\delta(NO_3)$, 1331 s $\delta(CH_3)$, 826 m-w $\nu(NO_3)$, 711 br,m $\delta(NH_2)$. 1H NMR in D_2O , δ : 0.79 (t, J 7.5 Hz, 3H, Me), 1.51 (sextet, J 7.5 Hz, 2H, CH_2), 2.26 (t, J 7.5 Hz, 2H, CH_2). $^{13}C\{^1H\}$ NMR in D_2O , δ : 12.4 (CH_3), 20.0 (CH_2), 34.0 (CH_2); the solubility of $n-PrC(=NH_2)NH_2^+NO_3^-$ is insufficient to observe the signal from $C=N$.

$n-BuC(=NH_2)NH_2^+NO_3^-$. Yield is 83% based on Co. Anal. Calcd for $C_5H_{13}N_3O_3$: C, 36.80; H, 8.03; N, 25.75. Found: C, 36.75; H, 7.71; N, 25.79. FAB⁺-MS, m/z : 101 $[M_{\text{cation}}]^+$, 201 $[2M_{\text{cation}} + H]^+$, 264 $[2M_{\text{cation}}]NO_3^+$, 427 $[3M_{\text{cation}} + 2NO_3]^+$. Mp = 190 °C. IR spectrum (KBr), selected bands, cm^{-1} : 3375 m-w and 3151 m-w $\nu(N-H)$, 2965 m-w $\nu(CH_3)$, 2873 w $\nu(CH_2)$, 1687 s $\nu(C=N) + \delta(NH_2)$, 1384 s $\delta(NO_3)$, 1320 s $\delta(CH_3)$, 802 s $\nu(NO_3)$, 730 br,m $\delta(NH_2)$. 1H NMR in D_2O , δ : 0.69 (t, J 7.0 Hz, 3H, Me), 1.16 (sextet, J_{apparent} 7.5 Hz, 2H, CH_2), 1.44 (quintet, J_{apparent} 7.4 Hz, 2H, CH_2), 2.25 (t, J 7.7 Hz, 2H, CH_2). $^{13}C\{^1H\}$ NMR in D_2O , δ : 12.9 (CH_3), 21.4 (CH_2), 28.4 (CH_2), 32.0 (CH_2); the solubility of $n-BuC(=NH_2)NH_2^+NO_3^-$ is insufficient to observe the signal from $C=N$.

$trans-[Co(MeCN)_2(H_2O)_4](NO_3)_2$. Anal. Calcd for $C_4H_{14}N_4CoO_{10}$: C, 14.25; H, 4.18; N, 16.62. Found: C, 13.96; H, 4.19; N, 15.34. FAB⁺-MS, m/z : 274 $[Co(MeCN)_2(H_2O)_4NO_3 - H]^+$ and 427 $[Co_2(MeCN)_4(H_2O)_8 + H]^+$. IR spectrum (KBr), selected bands, cm^{-1} : 3355 s, $\nu(H_2O)$, 2398 m-w $\nu(CN)$, 1627 s $\delta(H_2O)$, 1382 s $\delta(NO_3)$, 1048 w $\rho(CH_3)$, 827 s $\nu(NO_3)$, 660 s $\rho(O-H)$.

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