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Metal-catalysed carbon–carbon bond formation in the reaction of malononitrile with β-dicarbonyls

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Abstract

Nickel acetylacetonate effectively catalyses the carbon–carbon bond formation between malononitrile and β-dicarbonyls. In these metal-catalysed reactions malononitrile behaves as an electrophile towards the intercarbonylic carbon, so exhibiting a reverse reactivity compared with that one under basic or thermal conditions. The resulting organic products are β-cyanomethylene-β-enamino dicarbonyls (**2a–h**), which are obtained in good- to fair yield. β-Iminodicarbonyl complexes of nickel(II) and copper(II), which are likely intermediates in the catalytic cycle, are synthesised by reaction of the metal β-carbonylenolate with malononitrile or of the metal acetate with the catalysis product (**2a, d**).

Keywords: Malononitrile; β-dicarbonyls; Metal catalysis; Carbon–carbon coupling

1. Introduction

Coordination to metal centers not only can stabilise otherwise unstable organic fragments, but also can deeply modify their reactivity [1,2]. In this context we have found that the metal acts as a 'protecting group' toward the carbonyl function of coordinated β-dicarbonyls, so that, the oxygen of the C=O group appears in general rather unreactive. This fact represents a distinct advantage in terms of chemoselectivity, because, for example, electrophiles attack almost exclusively the methine carbon instead of the oxygen. An extensive application of this finding has been developed by us and involves the use of metal acetylacetonates as catalysts in the reactions of β-dicarbonyls with nitriles to give β-enaminodione derivatives [3,4].

In a preliminary communication we have also reported that the presence of catalytic quantities of $[Ni(acac)_2]$ can *reverse* the reactivities of malononitrile and β-dicarbonyls [5]. Under basic or thermal conditions, malononitrile behaves as a nucleophile *via* condensation of its methylene with the electrophilic carbonyl group

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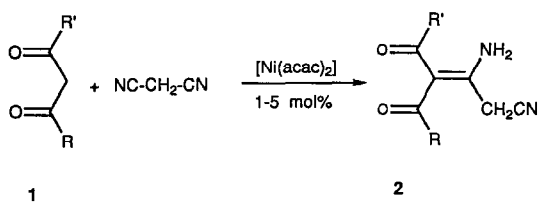
(Knoevenagel addition) [6,7]. By contrast, under metal catalysis the cyano carbon of malononitrile undergoes nucleophilic attack by the methylene carbon of β-dicarbonyl to give β-cyanomethylene-β-enaminodiones *via* carbon–carbon bond formation.

In this paper we report on: (i) full details on the synthesis and characterization of the organic products; (ii) the synthesis of metal complexes, possible intermediates in the catalytic cycle.

2. Results

2.1. Catalytic syntheses of β-cyanomethylene-β-enaminodiones from β-dicarbonyls and malononitrile

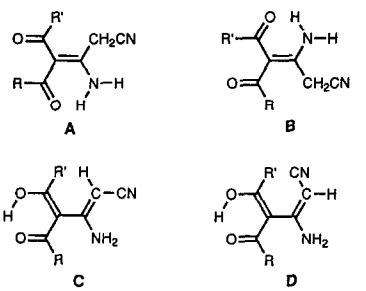
The reaction of β-diketones (**1a–c**) with malononitrile in the presence of catalytic amounts of [Ni(acac)$_2$] afforded the β-cyanomethylene-β-enaminodiones (**2a–c**) in 50–70% yield. Similarly dialkyl malonates (**1d–e**) gave β-cyanomethylene-β-enaminodiesters (**2d–e**) in 25–55% yield.



1 2

a: R = R' = Me; **b**: R = R' = Ph; **c**: R = Me, R' = Ph,
d: R = R' = OMe, **e**: R = R' = OEt

Compounds **2a–e** are characterised by strong infrared absorptions at: 3450–3200 (ν(N–H)), 2260–2200 (one band, ν(C≡N)] and 1680–1580 (ν(C=O), ν(C=C)) cm^{-1}. The ^{1}H NMR spectra of compounds **2b–e** show, as a rule, one signal of the methylene protons and two distinct resonances for the amino protons. This indicates that these compounds are present in solution as β-cyanomethylene-β-enamino dicarbonyls, with one C=O oxygen being involved in an hydrogen bond with the amino group (**A**, **B**). On the other hand compound **2a** exhibits in deuterated chloroform mainly in its enol forms (**C**, **D**; R = R' = Me) as



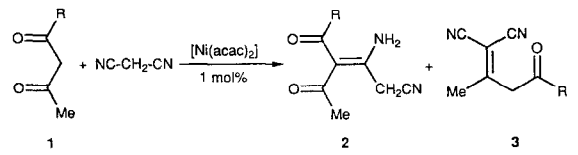
demonstrated by its NMR spectra. The protons show, in fact, absorptions at 16.5 and 16.6 ppm (two OH), 5.0 and 5.2 ppm (two broad NH$_2$), 3.84 and 3.98 ppm (two vinylic CH). The presence of vinylic CH is confirmed by two absorptions at 66.12 and 68.44 ppm (two doublets) in the ^{13}C NMR spectrum.

Yields markedly depend on the nature of the acetylacetonate metal catalyst, so that they range from good with cobalt(II) to low with zinc(II), whereas no product was obtained with [Cu(acac)$_2$]. No carbon–carbon bond formation was also observed in the reaction of acetylacetone (**1a**) with malononitrile in the presence of 1 mol% [Rh(acac)(CO)$_2$], which gives only the cyclic condensation product 3-cyano-4,6-dimethyl-2(1H)pyridone [7,8].

The reaction of β-ketoesters (**1f, g**) with malononitrile in the presence of catalytic amount of [Ni(acac)$_2$] afforded two different compounds: the β-cyanomethylene enaminoketoesters **2f, g** and the compounds **3f, g** derived from a Knoevenagel condensation and corresponding to the same compounds obtained in the base-promoted reactions [6,9,10].

In analogous experimental conditions the β-ketoamide **1h** gave the β-enaminoketoamide **2h** and the Knoevenagel derivative **3h.** In these

reactions compounds **3** were obtained in higher yield than compounds **2**.



f: R = OMe; g: R = OEt; h: R = $NHCH_2Ph$

The spectroscopic features of compounds **2f–h**, reported in Section 4, are similar to those illustrated above for compounds **2b–e** and correspond to the β-enaminodicarbonyl structures **A** and **B**.

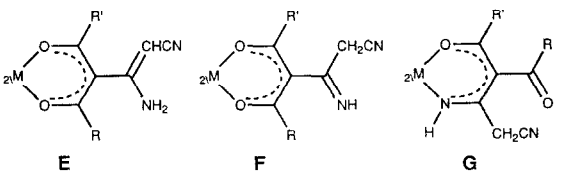
2.2. Synthesis of complexes, possible reactive intermediate in the catalytic cycle

The complexes have been synthesized with two alternative procedures. One involves the reaction of metal acetylacetonates with malononitrile in dichloromethane (Eq. (1)), the other is based on the ligand exchange reaction of metal acetates with 4-acetyl-3-amino-5-oxo-hex-3-enenitrile **2a** in ethanol (Eq. (2)).

$$[M(acac)_2] + NCCH_2CN \rightarrow [M\{(MeCO)_2CC(CH_2CN)NH\}_2] \quad (1)$$

$$M(OAc)_2 + (RCO)_2CC(CH_2CN)NH_2 \rightarrow [M\{(RCO)_2CC(CH_2CN)NH\}_2] + 2HOAc \quad (2)$$

Nickel acetylacetonate reacted with malononitrile to give a rather insoluble solvato complex (**4a**). Its infrared spectrum is characterised by: strong broad N–H stretching bands in the range 3440–3200 cm^{-1}, two $\nu(C\equiv N)$ absorptions at 2210 and 2180 cm^{-1} and a couple of bands at 1580 and 1520 cm^{-1}. The absence of any distinct absorption between 1700 and 1600 cm^{-1} indicates a great reduction of the C=O double bond character [11] and this would suggest coordination to nickel of both carbonyl groups (O,O coordination, **E** or **F**; R = R′ = Me) [12–14].



On the other hand, the low solubility and the overall feature of the infrared spectrum (very broad bands slightly changing in the various fractions of the complex) are consistent with strong intermolecular bonds to give oligomers; in this view it is possible that the very broad band centred at 1580 cm^{-1} contains the contributions of one metal-coordinated and of one uncoordinated carbonyl (**G**) involved in intermolecular interactions (hydrogen bonds). The reluctance to accept an O,O coordination is related to the fact that all β-iminocarbonylenolato complexes characterised by us show a general preference for N,O coordination [13,14]. However, the tendency of the protonated ligand **2a** to give the enolic forms **C** and **D**, not observed with other β-enaminodiones, may justify in this case the coordinating mode shown in **E**. An additional support to this hypothesis comes from the broad strong bands in the N–H stretching region of **4a**, which could be indicative of NH_2 groups involved in oligomeric chains. Despite of this structural problem, it clearly results that nickel acetylacetonate undergoes electrophilic attack at the methine carbon by the cyano carbon of malononitrile to form a new carbon–carbon bond.

The same reaction does not occur in the case of copper acetylacetonate even under drastic conditions (36 h at reflux in dichloroethane). To verify if the lack of reactivity of copper is due to an intrinsic instability of the final complex or to kinetic barriers, the synthesis of the β-iminodiketones of both nickel and copper was also run according to Eq. (2) i.e. employing the 'preformed' ligand. The nickel gave also in this

case a sparingly soluble complex (**4b**), which contains variable quantities of solvent. Its pale blue colour differs from the yellow–green one of complex **4a** obtained according to Eq. (1) and this may be indicative of a different set of chromophores. The infrared spectra of the two forms of the nickel complex are similar, apart from the absence in **4b** of the band at 1520 cm^{-1} and the significant presence of a band at 1630 cm^{-1}, of variable intensity in the various samples, which is attributable to a non-coordinated carbonyl [12,13] as in form **G**.

The procedure of Eq. (2) afforded the β-iminodiketonato complex also with copper (**5**), thus indicating that the failure of its synthesis according to Eq. (1) is due to a high kinetic barrier for the C–C bond formation. The complex precipitated from ethanol as a solvato violet solid with an infrared spectrum similar to that of the nickel analogue **4b** (coordination **G**, probably together with **E**). Treatment with dichloromethane gave a blue form, with markedly different infrared absorptions in the ν(N–H) and ν(C≡N) regions. Clearly the removal of the crystallisation molecules modified, in the case of the copper complex, the intermolecular interactions and perhaps the type of coordination. The broad absorptions at 3550–3230 cm^{-1}, typical of NH_2 groups (**E**), are replaced by two couples of sharp bands at 3480s, 3450s and 3360s, 3340s cm^{-1}, which seem more characteristic of coordinated =NH (**G**). The presence of four N–H stretching bands would indicate that the two imino groups have a different chemical environment and are probably involved in inter- and/or intramolecular hydrogen bonds. The existence of two ν(C≡N) bands is consistent with this hypothesis.

The procedure of Eq. (2) has been tested also with the (1-amino-2-cyano-ethylidene)-malonic acid dimethyl ester **2d**. Reaction of nickel acetate gives an untractable mixture without clear evidence of reaction, whereas copper acetate affords a blue complex with a very clean infrared spectrum, one single ν(N–H) band and one band at 1665 cm^{-1} characteristic of an uncoordinated ester group (N,O coordination, **G**).

3. Discussion

The results obtained demonstrate that [Ni(acac)$_2$] is a good catalyst that allows the formation of a new carbon–carbon bond between the intercarbonylic methylene and one of the cyano groups of malononitrile with formation of the β-enamino-dicarbonyls **2.** The reaction of β-diketones and of dialkyl malonates shows a high chemoselectivity to give compounds **2a–e**, also when their yields are low.

Low chemoselectivity is instead observed in the reactions of β-ketoesters **2f–g** and of the ketoamide **2h**. In these reactions compounds **3f–h**, derived from a typical base-promoted Knoevenagel reaction, are the main products while the metal catalyzed compounds **2f–h** are obtained generally in low yields.

Thus, the presence of a metal centre can modify the normal reactivity exhibited by malononitrile. The success of the carbon–carbon bond formation implies: (i) a specific electrophilic activation of the cyano carbon of malononitrile (via coordination to the metal) [15] and (ii) its interaction with a methine carbon nucleophilic enough to give C–C bond formation (Fig. 1) [16].

This stage of the catalytic cycle has been verified under stoichiometric conditions by re-

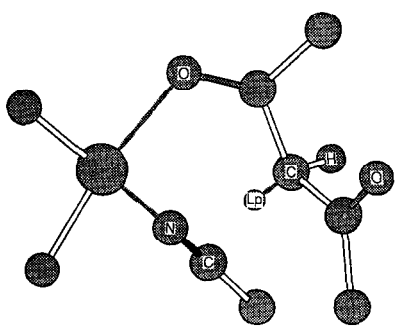


Fig. 1. Schematic drawing of the interaction of the methine lone pair with the cyano carbon of the coordinated nitrile. In this canonical formula the negative charge is fully located in the CH carbon.

acting [M(acac)$_2$] (M = Ni or Cu) with malononitrile in a 1:2 molar ratio. The reaction gives the expected β-iminocarbonylenolato complex only with nickel, whereas copper(II) is unreactive. There is, as a consequence, a good parallelism between catalytic activity of the metal centres and their ability to promote the carbon–carbon bond forming step [16]. Stable copper(II) β-iminocarbonylenolato complexes are, however, obtained by reaction of copper acetate with the convenient β-enaminodicarbonyls. This indicates that the lack of catalytic activity of copper(II) is not related to an intrinsic instability of the complex resulting from the C–C bond formation, but, rather, to a scarce efficiency of the metal centre in promoting this reaction.

This difference shown by the two metals may be related to the nature of the metal to ligand bonds in the corresponding β-carbonylenolato complexes: nickel has more ionic M–O bonds [17], this allows a greater negative charge on the methine carbon and a more nucleophilic character.

This last consideration, which relates the overall reactivity to the degree of negative charge on the methine carbon, can also be applied to the β-diesters, whose low reactivity can be attributed to a poorer C–H acidity than β-diketones [18].

The Knoevenagel reaction becomes important with β-ketoesters and β-ketoamides. In this case, the rate of thermal condensation of the methylene group of malononitrile with the carbonyl group of acetyl to give products **3** is comparable with the metal-catalyzed C–C bond formation (product **2**).

4. Experimental

4.1. Reagents and physical measurements

Metal acetates and acetylacetonates, β-diketones, β-diesters, β-ketoesters, malononitrile, solvents and gases were high purity commercial products and used as received. All syntheses were performed under nitrogen or argon. The following instruments were employed: a Perkin Elmer 781 Infrared, an AC 200 Bruker NMR spectrometer and a VG Micromass 16F spectrometer.

4.2. Catalytic syntheses from β-dicarbonyls and malononitrile

*4.2.1. Reaction of β-diketones (**1a–c**) with malononitrile*

General procedure:

*4.2.1.1. 4-Acetyl-3-amino-5-oxo-3-hexenenitrile **2a**.* To a solution of acetylacetone (**1a**) (1.0 g, 10 mmol) in chloroform (3 ml) [Ni(acac)$_2$] (0.03 g, 0.1 mmol) and malononitrile (0.73 g, 11 mmol) were added. The reaction mixture was heated under reflux for 6 h. The solvent was removed under reduced pressure to give yellow crystals of **2a**: 1.1 g (yield 66%), mp. 90–92°C (diethyl ether–light petroleum). Anal. Calcd. for $C_8H_{10}N_2O_2$: C, 57.82; H, 6.07; N, 16.86. Found: C, 57.90; H, 6.10; N, 16.95. IR (KBr, cm^{-1}): 3450, 3340, 3240, 2200, 1650, 1580. ^{1}H NMR ($CDCl_3$, δ, ppm): two isomeric ketoenol tautomers (**C** and **D**, R = R′ = Me) are present in a 3:2 ratio; the main isomer shows absorptions at 2.18 (s, 6H, 2 Me), 3.98 (s, 1H, CH), 5.2 (br, 2H, NH_2) and 16.5 (br, 1H, OH); the minor one at 2.22 (s, 6H, 2 Me), 3.84 (s, 1H, CH), 5.0 (br, 2H, NH_2) and 16.6 (br, 1H, OH). ^{13}C NMR ($CDCl_3$): main isomer, 22.76 (q, J = 128 Hz, 2 Me), 66.12 (d, J = 178 Hz, CH), 111.06 (s, *C*–CO), 118.63 (s, CN), 158.30 (s, C–NH_2), 190.97 (CO and C–OH); minor isomer, 22.53 (q, J = 128 Hz, 2 Me), 68.44 (d, J = 167 Hz, CH), 109.85 (s, *C*–CO), 120.30 (s, CN), 158.91 (s, C–NH_2), 191.14 (s, CO and C–OH).

According to this general procedure, the following compounds were obtained.

*4.2.1.2. 3-Amino-4-benzoyl-5-oxo-5-phenyl-3-pentenenitrile **2b**.* Obtained in 50% yield from dibenzoylmethane (**1b**) and malononitrile, by

stirring the reaction mixture in methylene chloride at room temperature for 10 d: colourless crystals, mp. 151–153°C. Anal. Calcd. for $C_{18}H_{14}N_2O_2$: C, 74.47; H, 4.86; N, 9.65. Found: C, 74.60; H, 4.90; N, 9.70. IR (KBr): 3360, 2240, 1635, 1590; ^{1}H NMR ($CDCl_3$): 3.8 (s, 2H, CH_2), 7.15–7.50 (m, 10H, 2 Ph), 8.7 (br, 1H, NH), 10.3 (br, 1H, NH).

4.2.1.3. 4-Amino-4-benzoyl-5-oxo-3-hexenenitrile ***2c***. Obtained in 70% yield from benzoylacetone (**1c**) and malononitrile, by stirring the reaction mixture in methylene chloride at room temperature for 10 d: colourless crystals, mp. 91–93°C. Anal. Calcd. for $C_{13}H_{12}N_2O_2$: C, 68.41; H, 5.30; N, 12.27. Found: C, 68.20; H, 5.40; N, 12.30. IR (KBr): 3410, 2260, 1645, 1600. ^{1}H NMR ($CDCl_3$): 1.83 (s, 3H, Me), 3.63 (s, 2H, CH_2), 6.6 (br, 1H, NH), 7.4–7.6 (m, 3H, Ph), 7.8–7.9 (m, 2H, Ph), 11.0 (br, 1H, NH). ^{13}C NMR ($CDCl_3$): 23.56 (t, $J = 137$ Hz, CH_2), 30.60 (q, $J = 127$ Hz, Me), 110.60 (s, C-4), 114.81 (s, CN), 128.92 (d, $J = 161$ Hz, Ph), 129.10 (d, $J = 161$ Hz, Ph), 133.43 (d, $J = 160$ Hz, Ph), 140.12 (s, Ph), 155.61 (s, C-3), 196.90 (s, CO), 197.00 (s, CO).

*4.2.2. Reaction of dialkyl malonates (**1d, e**) with malononitrile*

General procedure:

4.2.2.1. (1-Amino-2-cyano-ethylidene)-malonic acid dimethyl ester ***2d***. The reaction was carried out under two different experimental conditions.

Method A: To a solution of dimethylmalonate (1.28 ml, 10 mmol) in chloroform (5 ml) malononitrile (0.79 g, 12 mmol) and [Ni(acac)$_2$] (0.075 g, 0.3 mmol) were added. The reaction mixture was heated under reflux for 3 d, the solvent was removed under reduced pressure and the obtained oil was purified by flash chromatography (ethyl acetate–light petroleum 1:1). Compound **2d** was obtained as colourless crystals, mp. 85–87°C (chloroform–light petroleum), 0.44 g (yield 22%). Anal. Calcd. for $C_8H_{10}N_2O_4$: C, 48.49; H, 5.09; N, 14.14. Found: C, 48.87; H, 4.99; N, 14.28. IR (KBr): 3370 br, 3200, 2245, 1680, 1670, 1620; ^{1}H NMR ($CDCl_3$): 3.65 (s, 6H, 2 MeO), 3.82 (s, 2H, CH_2), 6.0–9.0 (br, 2H, NH_2).

Method B: To a solution of dimethyl malonate (0.64 ml, 5 mmol) in methanol (5 ml) malononitrile (0.37 g, 6 mmol) and [Ni(acac)$_2$] (0.064 g, 0.25 mmol) were added. The reaction mixture was stirred at room temperature for 3 d and then treated according to method A: compound **2d** was obtained in 50% yield.

4.2.2.2. (1-Amino-2-cyano-ethylidene)-malonic acid diethyl ester ***2e***. When the reaction was carried out in chloroform, heated under reflux for 2 h and then stirred at room temperature for 5 h, according to the method A, the compound **2e** was obtained in 46% yield as colourless crystals, mp. 55–58°C. Anal. Calcd. for $C_{10}H_{14}N_2O_4$: C, 53.09; H, 6.24; N, 12.38. Found: C, 52.63; H, 6.23; N, 12.79. IR (KBr): 3390, 3200, 2240, 1680, 1660, 1620; ^{1}H NMR ($CDCl_3$): 1.3 (t, $J = 8.0$ Hz, 6H, 2 Me), 3.88 (s, 2H, CH_2), 4.22 (q, $J = 8.0$ Hz, 4H, 2 CH_2O), 6.5–8.0 (br, 2H, NH_2).

When the reaction was carried out according to method B, compound **2e** was obtained in 53% yield.

*4.2.3. Reaction of alkyl acetoacetates (**1f, g**) with malononitrile*

General procedure:

A mixture of methylacetoacetate (1.1 ml, 10 mmol), malononitrile (0.79 g, 12 mmol) and [Ni(acac)$_2$] (0.025 g, 0.1 mmol) was heated in an oil bath at 50°C for 8 h. The reaction mixture was purified by flash chromatography (ethyl acetate–light petroleum 1:1) to give two main compounds:

4.2.3.1. 4,4-Dicyano-3-methyl-3-butenoic acid methyl ester ***3f***: . yellow oil, 0.96 g, yield 58%, Rf. 0.7. ^{1}H NMR ($CDCl_3$): 2.37 (s, 3H, Me), 3.68 (s, 2H, CH_2), 3.76 (s, 3H, OMe).

*4.2.3.2. 2-Acetyl-3-amino-4-cyano-2-butenoic acid methyl ester **2f**:* . colourless crystals, mp. 106–108°C, 0.40 g (yield 22%), Rf. 0.3. Anal. Calcd. for $C_8H_{10}N_2O_3$: C, 52.74; H, 5.53; N, 15.38. Found: C, 53.19; H, 5.56; N, 15.54. IR (KBr): 3300, 3150, 2240, 1740, 1680, 1610. ^{1}H NMR ($CDCl_3$): 2.38 (s, 3H, Me), 3.80 (s, 3H, OMe), 3.96 (s, 2H, CH_2), 6.0–7.0 (br, 1H, NH), 12.0–13.0 (br, 1H, NH)

When ethyl acetoacetate was reacted with malononitrile in the same experimental conditions two compounds were isolated:

*4.2.3.3. 4,4-Dicyano-3-methyl-3-butenoic acid ethyl ester **3g**:* . colourless oil [9,10], yield 58%, Rf. 0.65.

*4.2.3.4. 2-Acetyl-3-amino-4-cyano-2-butenoic acid ethyl ester **2g**:* . colourless crystals, mp. 96–97°C (chloroform–light petroleum), (yield 22%) Rf. 0.4. Anal. Calcd. for $C_9H_{12}N_2O_3$: C, 55.09; H, 6.16; N, 14.28. Found: C, 55.26; H, 6.25; N, 14.32. IR (KBr): 3300, 3150, 2240, 1740, 1685, 1620. ^{1}H NMR ($CDCl_3$): 1.3 (t, $J = 8.0$ Hz, 3H, Me), 2.33 (s, 3H, Me), 3.90 (s, 2H, CH_2), 4.22 (q, $J = 8.0$ Hz, 2H, CH_2O), 5.0–6.0 (br, 1H, NH), 10.0–12.0 (br, 1H, NH).

*4.2.4. Reaction of n-benzyl acetoacetamide (**1h**) with malononitrile*

To a solution of N-benzyl acetoacetamide (0.96 g, 5 mmol) in chloroform (4 ml), malononitrile (0.34 g, 5 mmol) and [Ni(acac)$_2$] (0.013 g, 0.05 mmol) were added. The reaction mixture was heated under reflux for 24 h, the solvent was removed under reduced pressure to give an oil which was purified by flash chromatography (ethyl acetate–light petroleum 1:1). Two main compounds were obtained:

*4.2.4.1. 4,4-Dicyano-3-methyl-3-butenamide N-benzyl **3h**.* Yellow crystal, mp. 99–102°C, 0.540 g (yield 45%), Rf. 0.65. Anal. Calcd. for $C_{14}H_{13}N_3O$: C, 70.28; H, 5.48; N, 17.56. Found: C, 70.46; H, 5.56; N, 17.45. IR (KBr): 3380, 3080, 2230, 1650, 1560, 1350, 1260; ^{1}H NMR ($CDCl_3$–DMSO-d_6 1:1): 2.35 (s, 3H, Me), 3.6 (s, 2H, CH_2), 4.36 (d, $J = 6.0$ Hz, 2H, NCH_2), 7.3 (m, 5H, Ar), 8.55 (br, 1H, NH).

*4.2.4.2. 2-Acetyl-3-amino-4-cyano-2-butenamide N-benzyl **2h**.* Colourless crystals, mp. 100–103°C (diethyl ether), 0.310 g (yield 24%), Rf. 0.3. Anal. Calcd. for $C_{14}H_{15}N_3O_2$: C, 65.36; H, 5.88; N, 16.33. Found: C, 64.72; H, 5.82; N, 15.96. IR (KBr): 3360, 2240, 1620, 1530, 1480; ^{1}H NMR ($CDCl_3$–DMSO-d_6 1:1): 2.11 (s, 3H, Me), 3.53 (s, 2H, CH_2), 4.47 (d, $J = 7.0$ Hz, 2H, NCH_2), 7.3 (m, 5H, Ph), 7.7 (br, 1H, NH), 8.2 (br, 2H, NH_2).

4.3. Synthesis of metal complexes

4.3.1. Reaction of nickel acetylacetonato with malononitrile

[Ni{$(MeCO)_2CC(CH_2CN)NH$}$_2$] (**4a**): $NCCH_2CN$ (0.20 g, 3 mmol) dissolved in carefully deoxygenated 1,2-dichloroethane (5 ml) was added under argon to [Ni(acac)$_2$] (0.26 g, 1 mmol in 5 ml of hot dichloroethane) and the resulting solution was kept at reflux for 1 h. Cooling to room temperature and reduction of the volume slowly afforded various fractions of a yellowish-green compound, which slightly differed in their infrared spectra and elemental analyses. One representative fraction contained about one mole of solvent per mole of complex. Anal. Calcd for $C_{18}H_{22}Cl_2N_4NiO_4$: C, 44.30; H, 4.54; N, 11.48. Found: C, 43.53; H, 4.25; N, 11.43. IR (KBr, cm^{-1}): 3440, 3320, 3200 [s, br ν(N–H)], 2210, 2180 [s, ν(C≡N)], 1580 [vs, br ν(C=O), ν(C=C)], 1520s, 1390 vs, br.

Copper acetylacetonate did not react with malononitrile in the same concentrations and prolonged reaction time (36 h at reflux).

4.3.2. Reaction of nickel and copper acetates with β-cyanomethylene-β-enaminodiones

*4.3.2.1. [Ni{$(MeCO)_2CC(CH_2CN)NH$}$_2$] (**4b**).* $Ni(OAc)_2 \cdot 4H_2O$ (0.25 g, 1 mmol) and $(MeCO)_2CC(CH_2CN)NH_2$ (**2a**, 0.34 g, 2 mmol)

were treated with ethanol (30 ml) under argon. The acetic acid was periodically removed with a moderate vacuum. After 2 h a pale blue solid was filtered off and washed with ethanol (3 ml). The compound is a solvato complex, which on the basis of the elemental analysis contains approximately 0.8 mol of ethanol and 1.2 mol of water (yield 75%). Anal. Calcd for $C_{17.6}H_{25.2}N_4NiO_6$: C, 47.24; H, 5.68; N, 12.52. Found: C, 46.40; H, 5.40; N, 12.00. IR (KBr, cm^{-1}): 3550, 3420, 3310 and 3200 [s, br ν(O–H), ν(N–H)], 2210m and 2180s [ν(C≡N)], 1630s [ν(C=O)], 1580vs, br [ν(C=O), ν(C=C)], 1390vs, br. This compound is almost insoluble in the usual organic solvents. Treatment with dichloromethane gives a solvato complex which contains approximately 0.2 mol of CH_2Cl_2 and 1 mol of H_2O. Anal. Calcd for $C_{16.2}H_{20.4}Cl_{0.4}N_4NiO_5$: C, 45.89; H, 4.85; N, 13.21. Found: C, 45.90; H, 4.86; N, 13.09. Its infrared spectrum is very similar to the previous one, the main difference being in the relative intensities of the C≡N stretching bands at 2210 and 2180 cm^{-1}.

4.3.2.2. [Cu{(MeCO)$_2$CC(CH$_2$CN)NH}$_2$] (5). $Cu(OAc)_2 \cdot H_2O$ (0.20 g, 1 mmol) and $(MeCO)_2CC(CH_2CN)NH_2$ (**2a**, 0.34 g, 2 mmol) were treated with ethanol (30 ml) under argon. After 1.5 h a violet solid was filtered off and washed with ethanol (3 ml). The compound is a solvato complex, which on the basis of the elemental analysis can be formulated as $[Cu\{(MeCO)_2CC(CH_2CN)NH\}_2] \cdot 0.8EtOH \cdot 0.2H_2O$ (yield 70%). Anal. Calcd for $C_{17.6}H_{23.2}CuN_4O_5$: C, 48.67; H, 5.38; N, 12.90. Found: C, 48.26; H, 5.25; N, 12.60. IR (KBr, cm^{-1}): 3550, 3430, 3335 and 3230 [s, br ν(O–H), ν(N–H)], 2180s [ν(C≡N)], 1630s [ν(C=O)], 1570vs, br [ν(C=O), ν(C=C)], 1450–1420s, br, 1380vs. This compound is almost insoluble in the usual organic solvents. Treatment with dichloromethane gives a solvato complex which contains approximately 0.1 mol of CH_2Cl_2. Anal. Calcd for $C_{16.1}H_{18.2}Cl_{0.2}CuN_4O_4$: C, 48.06; H, 4.56; N, 13.92. Found: C, 47.85; H, 4.48; N, 13.75. Its infrared spectrum shows important changes: 3480s, 3450s, 3360s, 3340s [ν(N–H)], 2200s and 2180s [ν(C≡N)], 1620s [ν(C=O)], 1570vs, br [ν(C=O), ν(C=C)], 1425sh, br, 1390vs, br cm^{-1}.

4.3.2.3. [Cu{(MeOCO)$_2$CC(CH$_2$CN)NH}$_2$] (6). $Cu(OAc)_2 \cdot H_2O$ (0.20 g, 1 mmol) and $(MeOCO)_2CC(CH_2CN)NH_2$ (**2d**, 0.40 g, 2 mmol) were treated with ethanol (30 ml) under argon. After 3 h a grey–green solid was filtered off and washed with ethanol (3 ml) (yield 45%). Anal. Calcd for $C_{16}H_{18}CuN_4O_8$: C, 41.97; H, 3.96; N, 12.24. Found: C, 42.48; H, 3.91; N, 12.29. IR (KBr, cm^{-1}): 3340s [ν(N–H)], 2210vw [ν(C≡N)], 1665s [ν(C=O)], 1580vs, br [ν(C=O), ν(C=C)], 1450s, 1430s, br, 1365vs. EI mass spectrum (m/z [identity]): 457(1) $[M]^+$, 425(1) $[M\text{-}CH_3OH]^+$, 410(1) $[M\text{-}CH_3OH\text{-}CH_3]^+$, 493(1) $[M-2CH_3OH]^+$, 198(30) $[HL]^+$, 167(90) $[HL-CH_3O]^+$, 166(100) $[HL-CH_3OH]^+$.

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