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## N,O *versus* O,O coordination in $\beta$ -imino diketonato complexes: Role of the metal center and of the imino substituent

Marino Basato<sup>a,\*</sup>, Marzio Bortolussi<sup>a</sup>, Elena Faggin<sup>a</sup>, Cristina Tubaro<sup>a</sup>, Augusto Cesare Veronese<sup>b</sup>

<sup>a</sup> Dipartimento di Scienze Chimiche, Università di Padova, and ISTM-CNR, Via Marzolo 1, I-35131 Padova, Italy <sup>b</sup> Dipartimento di Scienze Farmaceutiche, Via Fossato di Mortara 17, I-44100 Ferrara, Italy

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#### ABSTRACT

β-Imino carbonyl enolato metal(II) complexes of general formula [M((RCO)(R'CO)CC(R")NH)<sub>2</sub>] (M = Mn, Fe, Co, Ni, Cu, Zn, Pd, R = R' = Me, R" = CCl<sub>3</sub>; M = Cu, Pd, R = R' = Me, R" = PhCO; R = Me, R' = Ph, R" = PhCO; R = R' = Ph, R" = PhCO) are easily synthesized by the reaction of metal(II) acetates with the proper β-enaminodiones in 1/2 molar ratio in ethanol at room temperature. In all the cases the trifunctional NOO β-imino carbonyl enolate ligand acts as bidentate to give ML<sub>2</sub> complexes, whose structure depends on the metal center and on the nature of the substituent R" at the imino carbon. With R" = CCl<sub>3</sub> an O,O coordination is observed for all the metal centers but one, in fact palladium(II) exhibits an N,O coordination through the imino nitrogen and one keto oxygen. By contrast with R" = PhCO the ligand is always coordinated through the imino nitrogen and one keto oxygen atom.

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#### 1. Introduction

The use of acetylacetonato complexes of various transition metals as mild selective catalysts of C–C bond formation between C–H acid substrates and nitriles is a well-recognized procedure for the synthesis of substituted  $\beta$ -enaminones [1–4]. The scope of these products (RCO)(Z)C=C(R')NH<sub>2</sub> is quite large and involves the reaction of  $\beta$ -dicarbonyls (Z = RCO) [5],  $\beta$ -ketoamides (Z = C(O)NR<sub>2</sub>), nitroacetoesters (Z = NO<sub>2</sub>) [6],  $\beta$ -ketophosphonates (Z = PO(OR)<sub>2</sub>) [7] with nitriles bearing electron-withdrawing groups (R' = CN, CCl<sub>3</sub>, PhCO, CH<sub>2</sub>CN, ROCO). An extension of this synthetic procedure to non-activated nitriles (R' = alkyl, aryl, NH<sub>2</sub>) utilizes tin tetrachloride or cationic platinum nitrile complexes as promoters in stoichiometric quantity [8].

The mechanism implies in the key steps coordination of the nitrile to the metal center and consequent electrophilic activation of the cyano carbon, which undergoes nucleophilic attack by the C–H carbon of the enolato ligand. The resulting metal intermediate can adopt with  $\beta$ -carbonylenolato catalysts an N,O (linkage isomer I) or O,O coordination (linkage isomer II) (Chart 1).

These complexes were isolated in few cases by stoichiometric reaction of nickel(II) or copper(II) acetylacetonates with the proper nitrile (cyanogen or benzoyl cyanide) [9,10]. An alternative more general procedure, which avoids the occurrence of side reactions and/or decomposition pathways, involves the reaction of the metal

\* Corresponding author. Fax: +39 49 8275223.

E-mail address: marino.basato@unipd.it (M. Basato).

acetates with  $\beta$ -enaminodiones in ethanol at ambient temperature, and it has been mainly applied until now to the synthesis of  $\beta$ -imino carbonyl enolato complexes of Ni(II), Cu(II), Pd(II) of formula [M((MeOCO)(RCO)CC(R')NH)<sub>2</sub>] [11]. It should be underlined that an N,O coordination was always observed.

These compounds are alternative to  $\beta$ -diketonates as precursors in homogeneous and heterogeneous catalysis or in thin film chemical vapor deposition [12], so it seemed interesting to check this procedure with a more extended series of metal centers (Mn, Fe, Co, Ni, Cu, Zn, and Pd) and  $\beta$ -enaminodiones, in order to verify the generality of this synthesis and the type of coordination. The employed  $\beta$ -enaminodiones derive from the C–C coupling reaction of acetylacetone with trichloroacetonitrile, benzoyl cyanide, cyanogen and of benzoylacetone and dibenzoylmethane with benzoyl cyanide.

#### 2. Experimental

#### 2.1. Reagents and apparatus

The reagents were high purity products and generally used as received. Solvents were dried before use and the reaction apparatus was carefully deoxygenated. Reactions were performed under argon and all the operations were carried out under an inert atmosphere. The solution <sup>1</sup>H and <sup>13</sup>C{<sup>1</sup>H} NMR spectra were recorded on a Bruker 200AC (200.12 MHz for <sup>1</sup>H and 50.32 MHz for <sup>13</sup>C) or on a Bruker DRX 400 (400.13 MHz for <sup>1</sup>H and 100.63 MHz for <sup>13</sup>C); chemical shifts ( $\delta$ ) are reported in units of ppm relative to the





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residual solvent signals, using tetramethylsilane as the internal standard. The FT IR spectra were recorded on a Biorad FT S7 PC or on Bruker IFS 66 spectrophotometers at 2 cm<sup>-1</sup> resolution in KBr disks. Mass spectra were obtained with a single focus mass spectrometer VG MM16, operating in electron ionization mode at 70 eV electron beam energy and at an ion source temperature of 180 °C. TGS–DSC analysis was performed with Perkin–Elmer TGS-2, DSC-4 apparatus. Magnetic moments were determined by the Faraday method at 300 K using an Oxford Instruments magnet coupled with a Cahn 2000 microbalance. Elemental analysis was carried out at the microanalytical laboratory of our department with a Fisons EA 1108 CHNS-O apparatus.

#### 2.2. Synthesis of the ligands

The  $\beta$ -enaminodione (MeCO)<sub>2</sub>C=C(NH<sub>2</sub>)CCl<sub>3</sub> (**Hatpd**) (Chart 2) was prepared by the reaction of CCl<sub>3</sub>CN and 2,4-pentanedione in the presence of a catalytic amount of Ni(acac)<sub>2</sub> [13]. **Hatpo** was prepared by treatment of **Hatpd** with an alkaline solution [13]. The  $\beta$ -enaminodiones (MeCO)<sub>2</sub>C=C(COPh)NH<sub>2</sub> (**Haapd**), (Me-CO)(PhCO)C=C(COPh)NH<sub>2</sub> (**Habpd**) and (PhCO)<sub>2</sub>C=C(COPh)NH<sub>2</sub> (**Haopd**) were prepared according to the literature methods [14].

#### 2.3. Synthesis of the complexes

# 2.3.1. Reactions of $M(OAc)_2 \cdot nH_2O$ (M = Mn, Fe, Co, Ni, Cu, Zn, Pd) salts with 3-(1-amino-2,2,2-trichloroethylidene)pentane-2,4-dione (**Hatpd**) and with 4-amino-5,5,5-trichloropent-3-en-2-one (**Hatpo**): synthesis of complexes (**1-10**)

The reactions were performed by mixing the metal acetate and the protonated ligand in 1/2 molar ratio, in anhydrous ethanol, at room temperature under argon. Typically the metal salt (1 mmol) and **Hatpd** (or **Hatpo**) (2 mmol) were dissolved (or suspended) in 30 ml of deoxygenated ethanol. After 5 min, a precipitate began to separate and the reaction was completed in a few hours. The precipitate was collected by filtration, washed with ethanol and dried under vacuo. In the reaction with **Hatpo** the suspension was concentrated to a small volume before filtering, because of the greater solubility of the products. All these reactions may also be performed in acetone, but they require longer times due to the scarce solubility of the metal acetates in this solvent.

[Mn(**atpd**)<sub>2</sub>] (**1**): Light yellow solid (25% yield). M.p. 150 °C (dec.). *Anal.* Calc. for C<sub>14</sub>H<sub>14</sub>Cl<sub>6</sub>MnN<sub>2</sub>O<sub>4</sub> ( $M_W$  = 541.93): C, 31.03; H, 2.60; N, 5.17. Found: C, 30.01; H, 2.57; N, 4.87%. FTIR [cm<sup>-1</sup>, KBr]: 3237 [ $\nu$ (NH)], 1628 [ $\nu$ (C=N)], 1597 [ $\nu$ (MeC--O)]. Magnetic moment:  $\mu_{eff}$  = 6.0  $\mu$ B.

[Fe(**atpd**)<sub>2</sub>] (**2**): Light red solid (38% yield). M.p. 122 °C (dec.). *Anal.* Calc. for C<sub>14</sub>H<sub>14</sub>Cl<sub>6</sub>FeN<sub>2</sub>O<sub>4</sub> ( $M_W$  = 542.84): C, 30.98; H, 2.60; N, 5.16. Found: C, 30.75; H, 2.45; N, 5.13%. FTIR [cm<sup>-1</sup>, KBr]: 3233 [ $\nu$ (NH)], 1634 [ $\nu$ (C=N)], 1568 [ $\nu$ (MeC---O)]. Magnetic moment:  $\mu_{eff}$  = 5.1  $\mu$ B.

 $[Co(atpd)_2]$  (3): Light orange solid (54% yield). M.p. 146 °C (dec.). *Anal.* Calc. for C<sub>14</sub>H<sub>14</sub>Cl<sub>6</sub>CoN<sub>2</sub>O<sub>4</sub> ( $M_W$  = 545.93): C, 30.80; H, 2.58; N, 5.13. Found: C, 29.32; H, 2.39; N, 4.82%. FTIR [cm<sup>-1</sup>, KBr]: 3233 [ $\nu$ (NH)], 1628 [ $\nu$ (C=N)], 1593 [ $\nu$ (MeC---O)]. Magnetic moment:  $\mu_{eff}$  = 4.9  $\mu$ B.

[Ni(**atpd**)<sub>2</sub>] (**4**): Light green solid (73% yield). M.p. > 190 °C (dec.). *Anal.* Calc. for C<sub>14</sub>H<sub>14</sub>Cl<sub>6</sub>N<sub>2</sub>NiO<sub>4</sub> ( $M_W$  = 545.68): C, 30.81; H, 2.59; N, 5.13. Found: C, 30.83; H, 2.66; N, 4.97%. FTIR [cm<sup>-1</sup>, KBr]: 3234 [ $\nu$ (NH)], 1628 [ $\nu$ (C=N)], 1593 [ $\nu$ (MeC---O)]. Magnetic moment:  $\mu_{eff}$  = 4.1  $\mu$ B.

 $[Cu(atpd)_2]$  (5): Light blue solid (66% yield). M.p. 115 °C. *Anal.* Calc. for C<sub>14</sub>H<sub>14</sub>Cl<sub>6</sub>CuN<sub>2</sub>O<sub>4</sub> ( $M_W$  = 550.53): C, 30.54; H, 2.56; N, 5.09. Found: C, 30.44; H, 2.60; N, 4.89%. FTIR [cm<sup>-1</sup>, KBr]: 3236 [v(NH)], 1628 [v(C=N)], 1581 [v(MeC--O)]. Magnetic moment:  $\mu_{eff}$  = 1.9  $\mu$ B. The alcoholic mother liquor solution was evaporated to dryness and the residue was identified as the deacylated product [Cu(**atpo**)<sub>2</sub>] (**9**).

 $[Zn(atpd)_2]$  (**6**):  $Zn(OAc)_2 \cdot 2H_2O$  (0.20 g, 0.92 mmol) and **Hatpd** (0.45 g, 1.86 mmol) were dissolved in anhydrous ethanol (20 ml) and the resulting solution was stirred for 2 h at room temperature. The reaction mixture was concentrated to half of the volume and again stirred at room temperature for 2 h. Finally, the white insoluble reaction product was isolated by filtration and dried under vacuo (0.20 g, 39% yield). M.p. 161 °C. *Anal.* Calc. for C<sub>14</sub>H<sub>14</sub>Cl<sub>6</sub>N<sub>2</sub>O<sub>4</sub>Zn ( $M_W$  = 552.36): C, 30.44; H, 2.55; N, 5.07. Found: C, 30.10; H, 2.30; N, 4.55%. FTIR [cm<sup>-1</sup>, KBr]: 3237 [ $\nu$ (NH)], 1630 [ $\nu$ (C=N)], 1595 [ $\nu$ (MeC---O)]. <sup>1</sup>H NMR (in dmso-*d*<sub>6</sub>):  $\delta$  = 2.12 (s, 6H, CH<sub>3</sub>CO), 8.30 (s, 1H, CNH).

[Pd(**atpd**)<sub>2</sub>] (**7**): Yellow solid (45% yield). M.p. 150 °C (dec.). *Anal.* Calc. for C<sub>14</sub>H<sub>14</sub>Cl<sub>6</sub>N<sub>2</sub>O<sub>4</sub>Pd ( $M_W$  = 593.39): C, 28.34; H, 2.38; N, 4.72. Found: C, 27.16; H, 2.20; N, 4.46%. FTIR [cm<sup>-1</sup>, KBr]: 3331 [ $\nu$ (NH)], 1695 [ $\nu$ (MeC=O)], 1566 [ $\nu$ (MeC---O)]. <sup>1</sup>H NMR (in CDCl<sub>3</sub>):  $\delta$  = 2.10 and 2.59 (2s, 6H, CH<sub>3</sub>CO), 8.14 (s, 1H, CNH).



Hatpd:3-(1-amino-2,2,2-trichloroethylidene)pentane-2,4-dione

Hatpo: 4-amino-5,5,5-trichloropent-3-en-2-one

Haapd:3-acetyl-2-amino-1-phenylpent-2-ene-1,4-dione

Habpd: 2-amino-3-benzoyl-1-phenylpent-2-ene-1,4-dione

Haopd: 3-(1-amino-2-oxo-2-phenylethylidene)-1,5-diphenylpentane-1,2,4,5-tetraone

Haaon: 3-acetyl-2-amino-4-oxopent-2-enenitrile

[Ni(**atpo**)<sub>2</sub>] (**8**): Greenish solid (85% yield). M.p. 220 °C. *Anal.* Calc. for  $C_{10}H_{10}Cl_6N_2NiO_2$  ( $M_W = 461.61$ ): C, 26.02; H, 2.18; N, 6.07. Found: C, 26.08; H, 2.01; N, 6.33%. FTIR [cm<sup>-1</sup>, KBr]: 3340 [ $\nu$ (NH)], 1593 and 1516 [ $\nu$ (MeC---O),  $\nu$ (C---C) and  $\nu$ (C---N)]. <sup>1</sup>H NMR (in CDCl<sub>3</sub>):  $\delta$  = 1.87 (s, 3H, CH<sub>3</sub>CO), 5.55 (d, 1H, CH), 6.16 (br, 1H, CNH). <sup>13</sup>C NMR (in CDCl<sub>3</sub>):  $\delta$  = 25.3 (CH<sub>3</sub>CO), 92.2 (CH), 93.6 (CCl<sub>3</sub>), 162.5 (C(CCl<sub>3</sub>)), 182.3 (CH<sub>3</sub>CO).

[Cu(**atpo**)<sub>2</sub>] (**9**): Green solid (86% yield). M.p. 155 °C. *Anal.* Calc. for C<sub>10</sub>H<sub>10</sub>Cl<sub>6</sub>CuN<sub>2</sub>O<sub>2</sub> ( $M_W$  = 466.46): C, 25.75; H, 2.16; N, 6.01. Found: C, 25.71; H, 2.14; N, 5.85%. FTIR [cm<sup>-1</sup>, KBr]: 3347 [ $\nu$ (NH)], 1581 and 1523 [ $\nu$ (MeC---O),  $\nu$ (C---C) and  $\nu$ (C---N)]. Magnetic moment:  $\mu_{eff}$  = 1.7  $\mu$ B.

[Pd(**atpo**)<sub>2</sub>] (**10a,b**): Yellow solid (56% yield). M.p. ca. 170 °C. *Anal.* Calc. for C<sub>10</sub>H<sub>10</sub>Cl<sub>6</sub>N<sub>2</sub>O<sub>2</sub>Pd ( $M_W$  = 509.32): C, 23.58; H, 1.98; N, 5.50. Found: C, 22.59; H, 1.81; N, 5.34%. FTIR [cm<sup>-1</sup>, KBr]: 3343 and 3277 [ $\nu$ (NH)], 1588, 1580 and 1516 [ $\nu$ (MeC...O),  $\nu$ (C...-C) and  $\nu$ (C...-N)]. UV–Vis (CHCl<sub>3</sub>,  $\lambda_{max}/nm$ ,  $\varepsilon$  in parenthesis): 382 (9400), 240 (19100). MS-EI: m/z 508 ([Pd(atpo)<sub>2</sub>]<sup>+</sup>). The NMR spectra revealed that the isolated solid is a mixture of two compounds in approximately 1/1 ratio. Compound **10a**: <sup>1</sup>H NMR (in CDCl<sub>3</sub>):  $\delta$  = 2.09 (s, 3H, CH<sub>3</sub>CO), 5.58 (d, 1H, CH), 7.60 (s, 1H, CNH). <sup>13</sup>C NMR (in CDCl<sub>3</sub>):  $\delta$  = 25.9 (CH<sub>3</sub>CO), 91.6 (CH), 94.9 (CCl<sub>3</sub>), 160.8 (C(CCl<sub>3</sub>)), 182.8 (CH<sub>3</sub>CO). Compound **10b**: <sup>1</sup>H NMR (in CDCl<sub>3</sub>):  $\delta$  = 2.20 (s, 3H, CH<sub>3</sub>CO), 5.68 (d, 1H, CH), 6.68 (s, 1H, CNH). <sup>13</sup>C NMR (in CDCl<sub>3</sub>):  $\delta$  = 25.6 (CH<sub>3</sub>CO), 92.7 (CH), 95.1 (CCl<sub>3</sub>), 161.3 (C(CCl<sub>3</sub>)), 185.0 (CH<sub>3</sub>CO). Solutions of this mixture in CDCl<sub>3</sub> show a slow conversion of **10b** into **10a**.

2.3.2. Reactions of  $M(OAc)_2 \cdot nH_2O$  (M = Cu, Pd) salts with 3-acetyl-2amino-1-phenylpent-2-ene-1,4-dione (**Haapd**), 2-amino-3-benzoyl-1-phenylpent-2-ene-1,4-dione (**Habpd**), 3-(1-amino-2-oxo-2phenylethylidene)-1,5-diphenylpentane-1,2,4,5-tetraone (**Haopd**)

Complexes **11–16** were obtained by the reaction of the metal acetate with the appropriate protonated ligand in 1/2 molar ratio, in anhydrous ethanol, at room temperature under argon; the resulting solutions were left under stirring for variable times and the complexes can either precipitate spontaneously from the reaction mixture (for Cu, after 2–6 h) or be recovered from the solution evaporated to dryness (for Pd, after 3–18 h). In many cases the palladium compounds are isolable in two different forms, labeled as **a** and **b**, which exhibit identical composition but different spectroscopic properties; the symbols **a**, **b** indicate only the order in which the complexes have been isolated.

[Cu(**aapd**)<sub>2</sub>] (**11**): Light purple solid (71% yield). M.p. 194– 195 °C. *Anal.* Calc. for C<sub>26</sub>H<sub>24</sub>CuN<sub>2</sub>O<sub>6</sub> ( $M_W$  = 524.02): C, 59.59; H, 4.62; N, 5.35. Found: C, 59.69; H, 4.67; N, 5.27%. FTIR [cm<sup>-1</sup>, KBr]: 3254 [ $\nu$ (NH)], 1664 and 1650 [ $\nu$ (PhC=O)], 1617 [ $\nu$ (MeC=O)], 1597 [ $\nu$ (MeC--O)], 1556 [ $\nu$ (C---NH) and  $\nu$ (C---C)]. Magnetic moment:  $\mu_{eff}$  = 1.9  $\mu$ B.

 $[Pd(aapd)_2]$  (12a,b):  $[Pd(OAc)_2]$  (0.22 g, 1.0 mmol) and Haapd (0.46 g, 2.0 mmol) were dissolved in anhydrous ethanol (50 ml) and the resulting solution was stirred for 18 h at room temperature, then evaporated to a small volume under reduced pressure. The residue was treated with ethanol (10 ml) under stirring for 1 h and again the solvent was removed. This treatment was repeated three times. Finally, addition of ether (10 ml) gave a light green solid, which was filtered. Recrystallization from dichloromethane/acetone afforded pure 12a, as a yellow-green solid (0.29 g, 52%). M.p. 243–244 °C. Anal. Calc. for  $C_{26}H_{24}N_2O_6Pd$ (*M*<sub>W</sub> = 566.90): C, 55.09; H, 4.27; N, 4.94. Found: C, 55.02; H, 4.27; N, 4.99%. <sup>1</sup>H NMR (in CDCl<sub>3</sub>):  $\delta$  = 2.30 and 2.34 (2s, 6H, CH<sub>3</sub>CO), 7.2–7.9 (m, 6H, Ph and CNH). <sup>13</sup>C NMR (in CDCl<sub>3</sub>): δ = 27.7 (CH<sub>3</sub>CO), 31.5 (CH<sub>3</sub>CO), 116.9 ((CH<sub>3</sub>CO)C), 128.5-134.5 (Ph), 169.3 ((PhCO)CN), 185.1 (CH<sub>3</sub>CO), 190.4 (PhCO), 198.3 (CH<sub>3</sub>CO). FTIR [cm<sup>-1</sup>, KBr]: 3293 [v(NH)], 1676 and 1664 [v(PhC=O)], 1630 [v(MeC=O)], 1597 [v(MeC-O)], 1567 [v(C-NH) and v(C - C)]. MS-EI: m/z 566 ([Pd(**aapd**)<sub>2</sub>]<sup>+</sup>). The ethanol/ether solution, containing some **12a** and the more soluble form **12b**, was concentrated under vacuo; addition of hexane led to the precipitation of a mixture of complex **12b**, contaminated by some **12a**. Characterization of (**12b**). <sup>1</sup>H NMR (in CDCl<sub>3</sub>):  $\delta$  = 2.30 and 2.47 (2s, 6H, *CH*<sub>3</sub>CO), 7.2–7.9 (m, 6H, Ph and CN*H*). <sup>13</sup>C NMR (in CDCl<sub>3</sub>):  $\delta$  = 28.1 (*CH*<sub>3</sub>CO), 31.5 (*CH*<sub>3</sub>CO), 116.9 ((*CH*<sub>3</sub>CO)*C*), 128.5–134.5 (Ph), 169.9 ((PhCO)CN), 185.9 (CH<sub>3</sub>CO), 190.0 (PhCO), 198.0 (CH<sub>3</sub>CO).

 $[Cu(abpd)_2]$  (13): Green solid (84% yield). M.p. 215–216 °C. Anal. Calc. for C<sub>36</sub>H<sub>28</sub>CuN<sub>2</sub>O<sub>6</sub> ( $M_W$  = 648.16): C, 66.71; H, 4.35; N, 4.32. Found: C, 66.53; H, 4.34; N, 4.23%. FTIR [cm<sup>-1</sup>, KBr]: 3263 [ $\nu$ (NH)], 1675 and 1625 [ $\nu$ (PhC==O)], 1597 [ $\nu$ (MeC---O)], 1558 [ $\nu$ (C---NH) and  $\nu$ (C---C)]. Magnetic moment:  $\mu_{eff}$  = 1.9  $\mu$ B.

[Pd(**abpd**)<sub>2</sub>] (**14a**,**b**): [Pd(OAc)<sub>2</sub>] (0.22 g, 1.0 mmol) and **Habpd** (0.58 g. 2.0 mmol) were dissolved in anhydrous ethanol (50 ml) and the resulting solution was stirred for 20 h at room temperature, then evaporated to a small volume under reduced pressure. Treatment of the residue with diethylether (20 ml) afforded a light green solid, which was filtered, but resulted in a mixture of compounds 14a and 14b. Treatment with acetone (200 ml) led to an insoluble solid and a yellow solution. Recrystallization of the solid from dichloromethane/acetone afforded pure 14a, as a yellow-green solid (0.23 g, 33%). M.p. 258-259 °C. Anal. Calc. for  $C_{36}H_{28}N_2O_6Pd$  ( $M_W = 691.04$ ): C, 62.57; H, 4.08; N, 4.05. Found: C, 62.16; H, 4.09; N, 3.99%. <sup>1</sup>H NMR (in CDCl<sub>3</sub>):  $\delta$  = 1.85 (s, 3H, CH<sub>3</sub>), 7.2–7.9 (m, 6H, Ph and CNH). <sup>13</sup>C NMR (in CDCl<sub>3</sub>): δ = 27.2 (CH<sub>3</sub>CO), 113.2 ((CH<sub>3</sub>CO)C), 128.2–140.5 (Ph), 167.4 ((PhCO)CN), 183.8 (CH<sub>3</sub>CO), 191.9 (PhCO), 197.1 (PhCO). FTIR [cm<sup>-1</sup>, KBr]: 3261 [v(NH)], 1676 and 1630 [v(PhC=O)], 1597  $[v(MeC \dots O)]$ , 1565  $[v(C \dots C)$  and  $v(C \dots NH)]$ . The acetone solution was concentrated and the addition of diethylether led to the precipitation of a complex 14b, still containing small amounts of 14a. M.p. 270-272 °C. Anal. Calc. for C<sub>36</sub>H<sub>28</sub>N<sub>2</sub>O<sub>6</sub>Pd (M<sub>W</sub> = 661.04): C, 62.57; H, 4.08; N, 4.05. Found: C, 62.61; H, 4.07; N, 4.07%. <sup>1</sup>H NMR (in CDCl<sub>3</sub>):  $\delta$  = 1.52 (s, 3H, CH<sub>3</sub>CO), 7.25–7.95 (m, 11H, Ph and CNH). <sup>13</sup>C NMR (in CDCl<sub>3</sub>):  $\delta$  = 31.1 (CH<sub>3</sub>CO), 116.7 ((CH<sub>3</sub>CO)C), 128.2–140.5 (Ph), 170.0 ((PhCO)CN), 184.0 (PhCO), 191.0 (PhCO), 199.6 (CH<sub>3</sub>CO). FTIR [cm<sup>-1</sup>, KBr]: 3230 [v(NH)], 1676 [v(PhC=O)], 1644 and 1632 [v(MeC=O)], 1597 [v(PhC-O)], 1559 [v(C---C) and v(C---NH)].

[Cu(**aopd**)<sub>2</sub>] (**15**): Green solid (92% yield). M.p. 224–225 °C (dec). *Anal.* Calc. for C<sub>46</sub>H<sub>32</sub>CuN<sub>2</sub>O<sub>6</sub> ( $M_W$  = 772.30): C, 71.54; H, 4.18; N, 3.63. Found: C, 71.39; H, 4.33; N, 3.48%. FTIR [cm<sup>-1</sup>, KBr]: 3267 [ $\nu$ (NH)], 1663 and 1631 [ $\nu$ (PhC=O)], 1597 [ $\nu$ (PhC-O)], 1581 and 1547 [ $\nu$ (C---NH) and  $\nu$ (C---C)]. Magnetic moment:  $\mu_{eff} = 1.7 \ \mu$ B.

[Pd(**aopd**)<sub>2</sub>] (**16**): Green solid (62%). M.p. 270 °C. *Anal.* Calc. for C<sub>46</sub>H<sub>32</sub>N<sub>2</sub>O<sub>6</sub>Pd ( $M_W$  = 815.18): C, 67.78; H, 3.96; N, 3.44. Found: C, 67.37; H, 4.05; N, 3.29%. <sup>1</sup>H NMR (in dmso-*d*<sub>6</sub>): *δ* = 5.74 (br, 1H, CN*H*), 7.0–7.9 (m, 15H, Ph). FTIR [cm<sup>-1</sup>, KBr]: 3252 [*v*(NH)], 1662 and 1631 [*v*(PhC=O)], 1598 [*v*(PhC-O)], 1581 and 1557 [*v*(C---NH) and *v*(C---C)].

#### 2.3.3. Reactions of M(OAc)<sub>2</sub>·nH<sub>2</sub>O (M = Mn, Fe, Co, Zn) salts with 3acetyl-2-amino-1-phenylpent-2-ene-1,4-dione (**Haapd**) and 3-acetyl-2-amino-4-oxopent-2-enenitrile (**Haaon**)

Reactions of  $M(OAc)_2 \cdot nH_2O$  (M = Mn, Fe, Co, Cu, Zn, Pd) salts with 3-acetyl-2-amino-1-phenylpent-2-ene-1,4-dione (**Haapd**) or 3-acetyl-2-amino-4-oxopent-2-enenitrile (**Haaon**) were run using the metal acetate and the protonated ligand in 1/2 molar ratio, in anhydrous ethanol under various experimental conditions (room temperature, reflux), without any evidence of formation of the expected products. In some cases the starting aminodione underwent a cyclization reaction in the presence of the acetato salts.

#### 3. Results and discussion

The reaction of metal acetates with  $\beta$ -enaminodiones appears to be a convenient procedure for the synthesis of a large variety of  $\beta$ imino carbonyl enolato complexes; however, its applicability strongly depends on the nature of the substituent at the amino group and of the metal center, best results being obtained with the trichloromethyl derivative **Hatpd**.

3.1. Synthesis of complexes [*M*(*atpd*)<sub>2</sub>] (*M* = *Mn*, *Fe*, *Co*, *Ni*, *Cu*, *Zn*, *Pd*) (1-7) and [*M*(*atpo*)<sub>2</sub>] (*M* = *Ni*, *Cu*, *Pd*) (8–10)

Metal(II) acetates (M = Mn, Fe, Co, Ni, Cu, Zn, Pd) react in ethanol with 3-(1-amino-2,2,2-trichloroethylidene)pentane-2,4-dione **Hatpd** in 1:2 molar ratio to give the corresponding complexes **1–7** in a moderate yield (Scheme 1). They are generally air and moisture stable solids, which can be safely stored under an inert atmosphere, but they slowly decompose in solution and this accounts for the medium yields in the synthesis reaction.

In all the cases the trifunctional  $\beta$ -imino carbonyl enolate ligand acts as bidentate to give ML<sub>2</sub> complexes, whose structure depends on the metal center. For most metal centers the characterization data indicate an O,O coordination through the two carbonyl oxygens (linkage isomer **II**), whereas palladium(II) exhibits an N,O coordination through the imino nitrogen and one keto oxygen. In fact, the IR spectrum of complex **7** shows in particular a medium-high intensity N–H band at 3331 cm<sup>-1</sup> and a band at 1695 cm<sup>-1</sup> relative to the stretching of the uncoordinated C=O group. Consistently its <sup>1</sup>H and <sup>13</sup>C NMR spectra show the presence of two different sets of signals for the acetyl groups, as a consequence of the coordination of only one oxygen donor atom.

By contrast, the IR spectra of complexes 1-6 show rather different features; there is a band at 3237-3233 cm<sup>-1</sup> relative to the N-H stretching, but whose intensity is much weaker if compared with that found in complexes with N,O coordination. Moreover, only one absorption attributable to the stretching of the carbonyl groups is present at 1597–1568 cm<sup>-1</sup>, thus indicating a symmetric structure for the complexes with both the keto groups coordinated to the metal center. The band at 1634–1628 cm<sup>-1</sup> is easily attributed to an N-H stretching of uncoordinated imino group by D/H exchange experiments. Also the <sup>1</sup>H and <sup>13</sup>C NMR spectra for the diamagnetic complex (6) show a single set of signals for the acetyl groups, thus indicating a symmetric structure and the equivalency of the acetyl groups. The magnetic measurements for complexes  $[Mn(atpd)_2]$  (1),  $[Fe(atpd)_2]$  (2) and  $[Co(atpd)_2]$  (3),  $[Ni(atpd)_2]$ (4) and  $[Cu(atpd)_2]$  (5) show the presence of 5, 4, 3, 2 and 1 unpaired electrons, respectively, in agreement with the literature values [15]. Moreover, they suggest for complexes 1–4 an octahedral geometry for the metal centers resulting from an oligomeric structure with oxygen bridges, as already observed with acetylacetonates complexes [16].



Scheme 2. Synthesis of complexes 8-10.

All the complexes with the ligand **atpd** are thermally unstable, as indicated by the low melting points, always accompanied by the decomposition of the complex, by the very complex TGA–DSC curves and by the mass spectra, in which only low-mass fragments are present.

A possible decomposition pathway involves the deacylation of **atpd**, which is observed either with this synthetic procedure or in the direct attack of trichloroacetonitrile, for example, on copper acetylacetonate, so that we checked the coordinating ability of the deacylated ligand 4-amino-5,5,5-trichloropent-3-en-2-one **Hatpo** toward the same series of metal centers (Scheme 2).

Only a chelating N,O coordination is possible in this case, and both IR and NMR data are consistent with this configuration; in particular the <sup>13</sup>C resonances of the imino and keto carbon atom have ppm values in the expected range (162.5, 182.3 (**8**) and 160.8–161.3, 182.8–185.0 (**10a,b**)) for N,O coordinated imino carbonyl enolato complexes. The palladium complex is isolated in two isomeric forms **a** and **b**, the second one converting into the first one in solution, most likely as a consequence of a *cis–trans* equilibration. It is remarkable that Mn, Fe, Co, and Zn acetates do not react with this  $\beta$ -enaminone, and this point will be discussed later.

#### 3.2. Synthesis of complexes [*M*(*aapd*)<sub>2</sub>], [*M*(*abpd*)<sub>2</sub>], [*M*(*aopd*)<sub>2</sub>] (*M* = Cu, Pd) (11–16)

Metal(II) acetates of copper and palladium react in ethanol with the  $\beta$ -enaminodiketones **Haapd**, **Habpd**, and **Haopd** to give the corresponding bis(imino carbonyl enolato) complexes (**11–16**) (Scheme 3) in good yields. In most cases the complexes precipitate spontaneously, otherwise the reaction is forced toward the desired products by reducing the volume of the reaction mixture under vacuum; this procedure removes the solvent together with the acetic acid produced in the ligand exchange process.

Also with the benzoyl substituent at the imino carbon the N,O,O anionic ligand acts as bidentate to give monomeric square planar neutral  $ML_2$  complexes, in which the donor atoms are the imino nitrogen and a keto oxygen. The characterization of the complexes is made rather easy by a previous accurate IR and NMR study, including selective <sup>13</sup>C labeling, on the nickel(II) analogues [17]. The copper(II) complexes **11**, **13** and **15** are isolated only in one



Scheme 1. Synhesis of complexes 1-7.



Scheme 3. Synthesis of complexes 11-16.



Scheme 4. Procedures for the synthesis of β-imino carbonyl enolato complexes.

form and their IR spectra show characteristic absorptions in the expected wavelength ranges: in particular, 3367–3254 [one band, v(N-H)], 1675–1625 [one or two bands, v(PhC=O)], 1617 [one band, v(MeC=O) (11)], 1598–1597 [one band, v(MeC-O) (11, 13) or v(PhC-O) (15)] cm<sup>-1</sup>.

Palladium(II) complexes tend to give different forms, which are fairly stable both in the solid state and in solution. For example, the reaction of **Haapd** with palladium acetate allows the isolation of two different solids, labeled **12a,b**, with identical chemical composition but different spectroscopic features. The two forms have very similar IR and NMR spectra, fully consistent with the N,O linkage isomer **I** shown in Scheme 3; in particular both exhibit the typical signals of the coordinated and uncoordinated acetyl group. The small differences detected between the NMR spectra of **12a** and **12b** [for example, 27.7 and 31.5 (CH<sub>3</sub>CO), 185.1 and 198.3 (CH<sub>3</sub>CO) *versus* 28.1 and 31.5 (CH<sub>3</sub>CO), 185.9 and 198.0 (CH<sub>3</sub>CO)] could be attributable to the difference in the torsion angles of the substituents of the metal–carbonylenolate ring, as already observed in the analogous complex with nickel(II) [17] and in related  $\beta$ -imino carbonyl enolate palladium(II) complexes [11].

Also complex **14**  $[Pd(abpd)_2]$  is isolable in two forms **a** and **b**, which maintain an N,O coordination but differ in the oxygen donor atom, of the acetyl and benzoyl group, respectively. In fact, the <sup>13</sup>C NMR spectrum of **14a** shows the resonances typical of the coordinated MeC=O at 27.2 and 183.8 ppm to be compared with the values of 31.1 and 199.6 ppm of the uncoordinated one found in **14b**.

Attempts to apply this synthetic procedure to other metal acetates (M = Mn(II), Fe(II), Co(II) and Zn(II)) were unsuccessful. In particular in the reaction between Mn(II) acetate and **Haapd** the starting materials have been recovered unchanged, whereas using Fe(II), Co(II) or Zn(II) acetates under reflux, a cyclic compound, identified as 2-acetyl-3-amino-4-hydroxy-4-phenylcyclopent-2enone, has been isolated. The cyclization process occurs in the presence of free acetate anions in solution, as demonstrated by reaction of **Haapd** with NaOAc.<sup>1</sup> So it is reasonable to envisage that in the drastic conditions adopted, the Fe(II), Co(II) and Zn(II) acetates can partly dissociate thus realizing in solution an appreciable concentration of the base responsible for the cyclization.

In this context, it should be underlined that also the protonated cyano ligand **Haaon** does not react with the same set of metal acetates to give the desired imino carbonyl enolate complexes, but rather undergoes a cyclization reaction to give the cyclic pyrroline isomer [18].

The whole of the data obtained in this and in our previous papers gives a clear picture of the strategy to be adopted in the synthesis of  $\beta$ -imino carbonyl enolato complexes. The synthetic procedure depends markedly on the nature of the metal center and on the substituent at the imino carbon. The first applied procedure (i) involves electrophilic attack by the nitrile on the methine carbon atom of the coordinated  $\beta$ -carbonylenolato ligand (Scheme 4).

This C–C bond forming reaction requires nitriles bearing electron-withdrawing groups such as CN, CCl<sub>3</sub>, and PhCO and, in addition, metal centers with an ionic character of the M–O bond in the chelate ring [19]: this last point explains, for example, why Pd(II), Cr(III) and Fe(III) acetylacetonates are completely unreactive also toward very electrophilically activated nitriles [20]. In general, the control of the reaction conditions is very delicate, so that espe-

<sup>&</sup>lt;sup>1</sup> A solution of **Haapd** (0.12 g, 0.5 mmol) and NaOAc (0.04 g, 0.5 mmol) in ethanol (25 ml) was refluxed for 10 h and then further stirred at room temperature for 18 h. The solvent was removed under vacuo and the residue recrystallized from dichloromethane/diethylether. The resulting off-white product was isolated by filtration and dried (0.10 g, 82% yield). M.p. 187–189 °C. *Anal.* Calc. for C<sub>13</sub>H<sub>13</sub>NO<sub>3</sub> ( $M_{\rm W}$  = 231.15): C, 67.52; H, 5.67; N, 6.06. Found: C, 67.53; H, 5.66; N, 6.05%. FTIR [cm<sup>-1</sup>, KBr]: 3355 and 3216 [v(NH) and v(OH)], 1684, 1635, 1608 and 1529 [v(C=O) and v(C=C)]. <sup>1</sup>H NMR (in dmso-d<sub>6</sub>):  $\delta$  = 2.37 (s, 3H, CH<sub>3</sub>CO), 2.65 (AB system, 2H, CH<sub>2</sub>), 6.37 (s, 1H, OH), 7.34 (br, 5H, Ph), 8.47 and 9.09 (s, 2H, CNH). <sup>13</sup>C NMR (in dmso-d<sub>6</sub>):  $\delta$  = 82.88 (CH<sub>3</sub>), 53.0 (CH<sub>2</sub>), 75.3 (C(OH)Ph), 109.0 ((CH<sub>3</sub>CO)C), 124.4–144.1 (Ph), 182.8 (CN), 195.0 and 195.7 (CO).

cially in the reaction of cyanogen with the more ionic acetylacetonates (M(II) = Mn, Fe, Co, Zn) the initially formed complexes are very reactive and evolve to complex mixtures [21]. By contrast benzoyl cyanide requires high temperatures in which the complexes may be unstable, and this markedly reduces the yields. Good results have been obtained with Ni(II), Cu(II) and, in part, with Zn(II).

The second more recent procedure (ii) implies reaction of the metal acetates with the "preformed" β-enaminodione in an exchange process. Clearly, the position of this equilibrium is determined by the relative acidities of the  $\beta$ -enaminodione and HOAc, and by the stabilities of the acetato salts and β-imino carbonyl enolato complexes. β-Enaminodiones with a trichloromethyl substituent at the imino carbon are very acidic and react with all the investigated metal acetates: the coordination is N.O only for the soft palladium(II). The situation markedly changes in the β-enaminodiones derived from benzovl cvanide: in fact, good results are obtained only with Ni(II), Cu(II) and Pd(II), and under forced conditions only cyclization of the ligand is observed. Quite remarkably, N,O coordination is observed in this case also for Ni(II) and Cu(II) metal centers, so underlining their borderline hard-soft character. In conclusion, procedure (ii) has a good generality regarding the type of imino substituent. However, sometimes it is limited with hard metal centers, when the low acidity of the  $\beta$ -enaminodione with respect to the acetic acid is not compensated by a slightly greater stability of the β-imino carbonyl enolato complex with respect to the starting acetato salt. This phenomenon is particularly evident in the reaction of the N,O bidentate Hatpo with metal acetates; in fact only the softer Ni(II), Cu(II) and Pd(II) undergo exchange of the hard 0,0 acetate ligand.

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#### References

- [1] E.C. Constable, Metals and Ligand Reactivity, VCH, Weinheim, 1995.
- [2] N.S. Simpkins (Ed.), 100 Modern Reagents, The Royal Society of Chemistry,
- London, 1989. [3] B. Corain, M. Basato, A.C. Veronese, J. Mol. Catal. 81 (1993) 133.
- [4] (a) T. Hashimoto, S. Hara, Y. Shiraishi, M. Yamauchi, K. Natarajan, K. Shimizu, Inorg. Chim. Acta 358 (2005) 2207;

(b) T. Hashimoto, S. Hara, Y. Shiraishi, M. Yamauchi, K. Natarajan, K. Shimizu, Chem. Lett. 32 (2003) 874;

(c) Y. Nakano, T. Noguchi, H. Kondo, T. Ishiwata, S. Sato, Inorg. Chim. Acta 358 (2005) 513;
(d) T. Uchiyama, K. Takagi, K. Matsumoto, S. Ooi, Y. Nakamura, S. Kawagucthi,

- Bull. Chem. Soc. Jpn. 54 (1981) 1077.
- [5] B. Croxtall, E.G. Hope, A.M. Stuart, Chem. Commun. (2003) 2430.
- [6] M. Basato, N. Detomi, M. Meneghetti, A.C. Veronese, R. Callegari, J. Mol. Catal. A: Chem. 139 (1999) 121.
- [7] A.C. Veronese, R. Callegari, J. Mol. Catal. 68 (1991) L1.
- [8] (a) A.C. Veronese, V. Gandolfi, M. Basato, B. Corain, J. Chem. Res. (S) (1988) 246;
  (b) A.C. Veronese, V. Gandolfi, M. Basato, B. Corain, J. Chem. Res. (M) (1988) 1843;
  (c) M.E. Cucciolito, V. De Felice, F. Giordano, I. Orabona, F. Ruffo, Eur. J. Inorg.

(c) M.E. Cucciolito, V. De Felice, F. Giordano, I. Orabona, F. Ruffo, Eur. J. Inorg. Chem. (2001) 3095.

- [9] M. Basato, B. Corain, G. Zanotti, J. Chem. Soc., Dalton Trans. (1992) 3003.
- [10] M. Basato, U. Casellato, R. Graziani, A.C. Veronese, J. Chem. Soc., Dalton Trans. (1992) 1193.
- [11] M. Basato, U. Vettori, A.C. Veronese, A. Grassi, G. Valle, Inorg. Chem. 37 (1998) 6737.
- [12] F.D. Lewis, A.M. Miller, G.D. Salvi, Inorg. Chem. 34 (1995) 3171, and references cited therein.
- [13] A.C. Veronese, C. Talmelli, V. Gandolfi, B. Corain, M. Basato, J. Mol. Catal. 34 (1986) 195.
- [14] M. Basato, B. Corain, M. Cofler, A.C. Veronese, G. Zanotti, J. Chem. Soc., Chem. Commun. (1984) 1593.
- [15] A.F. Orchad, Magnetochemistry, Oxford University Press, Oxford, 2003.
- [16] R.C. Mehrotra, R. Bohra, D.P. Gaur, Metal β-Diketonates and Allied Derivatives, Academic Press, New York, 1978.
- [17] M. Basato, G. Favero, A.C. Veronese, A. Grassi, Inorg. Chem. 32 (1993) 763.
- [18] M. Basato, B. Corain, A.C. Veronese, F. D'Angeli, G. Valle, G. Zanotti, J. Org. Chem. 49 (1984) 4696.
- [19] M. Basato, B. Corain, V. Gandolfi, A.C. Veronese, J. Chem. Soc., Dalton Trans. (1988) 1213.
- [20] B. Corain, C. Crotti, A. Del Pra, F. Filira, G. Zanotti, Inorg. Chem. 20 (1981) 2044.
- [21] B. Corain, M. Basato, A. Marcomini, Inorg. Chim. Acta 74 (1983) 1.