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Complexation of Chiral Di (*N*-Protected α-Amino)-β-Diketones with Some Transition Metals

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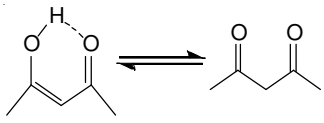
Chiral Di (*N*-protected α-amino)-β-diketones and its transition metal complexes have been synthesized. Di(*N*-protected α-amino)-β-diketones were prepared by reaction of activation of *N*-protected- α-amino acids (imidazolide) with α-diazoketones derived from natural amino acids in presence of lithium diisopropyl amid in tetrahydrofuran as a solvent at -78 ºC and treatment the product with rhodium acetate to remove diazo group. The synthesized compounds were characterized by analytical techniques *viz*: IR, NMR and elemental analysis. The thermal stability of the newly synthesized metal complexes have been studied.

Key Words: Protecting mino acid, Diazomethane, β-Diketones, Carbonyldiimidazol metal ions.

INTRODUCTION

β-Diketones are used as ligands for almost 120 years. These derivatives were synthesized for the first time in 1887. The nature of bonding and chelation was elucidated by Werner and Morgan[1,2]. In the last decades, β-diketones and their metal complexes have been used as model compounds in physical chemistry studies. They have also been used as chelating ligands for lanthanides and transition metals[3]. They are bidentate ligands with the possibility of complexation with almost all the metal ions[4]. β-Diketones have a wide range of uses in metal extraction by chelation. 1,3-Diketones are very important compounds in organic chemistry, because they exhibits some biological activities, such as antioxidants, anti-tumor and antibacterial activities and are also key intermediates to various heterocyclic compounds[5,6].

β-Diketone in its keto-enol form is also a important used as chelating agents in some process based on supercritical CO_2[7]. It is used as extractants for lanthanide ions[8]. β-Diketones (1,3-ketones), such as acetylacetone, are particularly prone to form stable enols or enolates because of conjugation of the enol or enolate with the other carbonyl group and the stability gained in forming a six-membered ring, (hydrogen bonded in the case of the enol or containing the counter ion in the case of the enolate).



The conjugate base derived from 1,3-ketones form complexes with metal ions. Diketones with one or two methylene groups separating the carbonyl groups typically coexist with their enol tautomers. The reactions of such dicarbonyls are very similar to those of simple ketones.

In the last years many scientific papers have been published on synthesis of *N*-protected α-amino acid, α-diazoketones and α-diazoketoles derived from natural amino acids by several methods[9]. A series of *N*-protected α-aminodiazoketones has been prepared from L-amino acids and dipeptides and used as precursors in the synthesis of *N*-protected α-amino -β-diketones[10]. The synthesis of α-amino protected acyldiazomethanes involves the activation of the carboxyl group of *N*-protected-α-amino acids followed by acylation of diazomethane. The acid chloride[11] active ester[12] and the mixed anhydride methods[13] have been employed for the activation. The acid chloride method is not applicable for some protecting groups because of the acid lability or oxazolone formation.

α-Diazocarbonyls ($RCOCHN_2$) have an acidic hydrogen on the methine group and readily removed by strong base to furnish a nucleophilic anion capable to condensation[14] with activation *N*-protected amino acids[15] to get high yields of diazo-β-diketons. Lithium diisopropylamine (LDA) is the base of choice when highly yields of condensation of α-diazocarbonyls with activation *N*-protected amino acids. Carponyldiimidazol (CDI) is a suitable activation group of *N*-protected amino acids to produce imidazolide[16-19]. This imidazolide was treated directly with diazolithio-ketones to get high percentage yield of diazo-β-diketons. Rhodium-catalyst[20] was subsequent to preparation of novel di(*N*-protected α-amino)-β-dicarbonyl compounds then complexation with some metal ions [Cu(II), Ni(II) and Fe(III)].

EXPERIMENTAL

Reactions requiring anhydrous conditions were performed in flame-dried glassware under a positive pressure of nitrogen. Reaction mixtures were stirred magnetically. Air -and moisture-sensitive liquids and solutions were transferred *via* syringe or cannula into the reaction vessels through rubber septa. Column chromatography was performed using Rhon-poulenc silica gel C60-H (40-60μm).

Commercial grade solvents were used without purification except as indicated below. Tetrahydrofuran was distilled from sodium benzophenone dianion, dichloromethane. Diis opropylamine was purified by molecular seives then distillation, *n*-butyllithium (1.6 M solution in hexane) was purchased from across, 1,1'-carbonyldiimidazole, *N*-benzyloxycarbonyl-L-alanine, *N*-benzyloxycarbonyl-L-valine and *N*-benzyloxy-carbonyl-L-phenylalanine, were purchased from acros, N_2 gas was dried over copper pieces, silica gel and molecular sieve. The hexane and ethyl acetate used for chromatography were purified by distillation. Infrared spectra were recorded as KBr-discs on Matsson 5000-FTIR spectrophotometer within the range of 4000-500 cm^{-1}, ^1H and ^{13}C-NMR were recorded on Bruker AC 300 MHz and AC 75 MHz respectively.

Preparation of diazomethane (CH_2N_2): Ethereal di-azomethane was prepared from toluene-*p*-sulphonyl chloride and methylamine in alkaline solution according to the literature procedure[21]. [CH_2N_2 may explode in contact with sharp edges, such as ground-glass joints, even scratches in glassware]. Glassware should be inspected before use and preparation should take place behind a blast shield. Specialized kits to prepare diazomethane with flame-polished joints are commercially available. The compound explodes when heated beyond 100 ºC. it is a extremely sensitive explosive yellow gas, thus it is almost universally used as a solution in diethyl ether.

General procedure for α-diazoketones preparation *via* mixed anhydrides: The *N*-protected amino acid (27.0 mmol) in dry Et_2O (60 mL) and THF (60 mL) was stirred at -20 ºC under a nitrogen atmosphere. To this solution, Et_3N (3.8 mL, 1 equiv.) followed by isobutyl chloroformate (3.7 mL, 1 equiv.) were added. The solution was stirred for 0.5 h and then allowed to warm to -10 ºC. At this temperature etheral CH_2N_2 (2 equiv), was added *via* a pressure equalizing dropping funnel over 0.5 h. The solution was stirred for a further 3 h whilst warming to room temperature. The mixture was evaporated to a third of its original volume using a rotary evaporator with an AcOH trap to destroy residual CH_2N_2.The solution was diluted with Et_2O (50 mL) and washed with H_2O (50 mL), saturated aqueous $NaHCO_3$ (50 mL) and brine (50 mL). The organic fraction was dried and evaporated to give the crude α-diazoketone which was purified by silica gel chromatography (EtOAc-hexane 2:8-3:7).

Benzyl [(2*R*)-4-diazo-3-oxobutan-2-yl]carbamate (4): Following the general procedure *N*-benzyloxycarbonyl-l-alanine **1** (27 mmol, 6 g) was converted into title compound **4**. Purification using EtOAc-hexane as eluent funished the diazoketone **4** (5.7 g, 84 %) as a pale-yellow solid. m.p. 90-91 ºC, $[\alpha]^{20}_D$ = -59.08 (c 1, MeOH). Found: C 58.2; H 5.22; N 16.98 %. $C_{12}H_{13}N_3O_3$ requires C 58.3; H 5.3; N 17.0 %. (KBr, ν_{max}) 3315 (NH), 2105 (CHN_2), 1722 ($NHCO_2Bnz$), 1645 cm^{-1} ($COCHN_2$). ^1H NMR (300 MHz, $CDCl_3$): δ = 1.21 (3H, d, *J* = 7.1 Hz, CH3CH), 4.30 (1H, m, CH(N)CO), 5.20 (2H, s, OCH_2Ph), 5.54 (1H, br s, CHN_2), 5.76 (1H, br, s, NH), 7.26-7.35 (5H, m, ArH). ^{13}C NMR (75 MHz, $CDCl_3$): δ = 18.5, 53.7, 54.5, 67.1, 128.2, 128.3, 128.6, 136.4, 155.9, 194.1.

Benzyl [(3*R*)-1-diazo-4-methyl-2-oxopentan-3-yl]-carbamate (5): *N*-Benzyloxycarbonyl-*l*-valine (**2**) (27 mmol, 6.8 g) was converted into title compound (**5**). Purification using EtOAc-hexane as eluent funished the pure diazoketone **5** (5.17 g, 75 %) as a yellow solid m.p 30-31 ºC, $[\alpha]^{20}_D$ = -31.5 (c 1, MeOH). Found: C 61.05; H 6.19; N 15.2 %. $C_{14}H_{17}N_3O_3$ requires C 61.1; H 6.2; N 15.3 %. (KBr, ν_{max}) 3330 (NH); 2110 (CN_2); 1725 (CO_2CH_2Ph); 1635 cm^{-1} ($COCHN_2$. ^1H NMR (300 MHz, $CDCl_3$): δ = 0.87-0.99 (6H, d, *J* = 6.75 Hz, -$CH(CH_3)_2$); 2.15 (1H, m, -$CH(CH_3)_2$); 4.45 (1H, m, -N-CH-CO-); 5.17 (2H, s, CH_2Ph); 5.41 (1H, br, NH); 5.42 (1H, s, CHN_2); 7.40 (5H, s, phenyl group). ^{13}C NMR (75 MHz, $CDCl_3$): δ = 17.4, 19.5, 31.2, 54.8, 63.0, 67.1, 128.1, 128.2, 128.6, 136.3, 156.5.

Benzyl [(2*R*)-4-diazo-3-oxo-1-phenylbutan-2-yl]-carbamate (6): *N*-Benzyloxycarbonyl-*l*-phenylalanine (**3**) (27 mmol, 8.1 g) was converted into title compound (**6**). Purification using EtOAc-hexane as eluent funished the pure diazoketone **6** (6.40 g, 88 %) as a yellow solid m.p. 80-81 ºC, $[\alpha]^{20}_D$ = -42.1 (c 1, MeOH). Found: C 66.69; H 5.25; N 12.93 %. $C_{18}H_{17}N_3O_3$ requires C 66.9; H 5.3; N 13.0 %. ºC. (KBr, ν_{max}) 3322 (NH); 2106 (CHN_2); 1696 (CO_2-bnz); 1635 cm^{-1} ($COCHN_2$). ^1H NMR (300 MHz, $CDCl_3$): δ = 3.03 (2H, d, *J* = 6.85 Hz, $PhCH_2$); 4.45 (1H, m, CHNCO); 5.21 (2H, s, O-CH_2Ph); 5.31 (1H, s, CHN_2); 5.35 (1H, br, NH); 7.18-7.42(10 H, m, ArH). ^{13}C NMR (75 MHz, $CDCl_3$): δ = 38.31, 54.4, 58.7, 66.9, 127.0, 127.9, 128.1, 128.4, 128.5, 129.2, 135.9, 136.0,155.6, 192.6.

Synthesis of N-Protected-α-amino acids imodazolide

Benzyl [(2*R*)-1-(1*H*-imidazol-1-yl)-1-oxopropan-2-yl]-carbamate (7): To a stirred solution of **1** (3.80 g, 17.2 mmol) in dry THF (50 mL), carbonyldiimidazole (CDI) (3.07 g, 18.9 mmol) was added under nitrogen at 25 ºC. After stirring for 2 h at 25 ºC the alaninylimidazolide was obtained and used directly in the next step without isolate and further purification.

Benzyl [(3*R*)-1-(1*H*-imidazol-1-yl)-3-methyl-1-oxobutan-2-yl]carbamate (8): 4.75 g, of *N*-benzyloxycarbonyl-*l*-valine (17.2 mmol) and (3,07 g, 18.9 mmol) CDI in THF were reacted according to the same procedure employed in compound (**7**) and used directly in the next step without further purification.

Benzyl [(2*R*)-1-(1*H*-imidazol-1-yl)-1-oxo-3-phenyl-propan-2-yl]carbamate (9): 5.32 g, of *N*-benzyloxycarbonyl -l-phenylalanine (17.2 mmol) and (3,07 g, 18.9 mmol) CDI in THF were reacted according to the same procedure employed in compound (**7**) and used directly in the next step without further purification.

Synthesis of 2-diazo-1,3-diketones derived from amino acids

Dibenzyl [(2*R*, 6*R*)-4-diazo-3,5-dioxoheptane-2,6-diyl]carbamate (10): A cold (-78 ºC) solution of lithium diisopropylamine (10.8 mL of a 1.6 M solution in cyclohexane, 17.2 mmol) was added over 15 min under nitrogen *via* syringe to a stirred solution of carbamate **4**, (2.13 g, 8.60 mmol) in dry THF (30 mL) at -78 ºC. A solution of imidazolide **7** was

added dropwise over 15 min under nitrogen *via* cannula at such a rate so as to keep the temperature below -78 ºC and stirring was continued for an additional 2 h. Acetic acid (12 µL, 17.2 mmol) in dry THF (5 mL) was added. The mixture was allowed to warm to room temperature and H_2O (20 mL) was added. The product was extracted with Et_2O (3 × 50 mL) and the combined organic extracts washed with saturated aqueous $NaHCO_3$ (50 mL) and brine (50 mL), dried over anhydrous Na_2SO_4 and concentrated under reduced pressure to give a brown oil. Purification by column chromatography using EtOAc:*n*-hexane (3:7) as eluent furnished the title compound **10** (2.996 g, 77 %) as a yellow oil. Anal. calcd. for $C_{23}H_{24}N_4O_6$ C 61.06, H 5.35, N 12.38 %. Found: C, 60.99 ; H, 5.21; N,12.24 %. (KBr, ν_{max}) 3315 (NH); 2099 (CN_2); 1705 (CO_2CH_2); 1631 ($COCN_2$);1520 cm^{-1} (Ph). ^1H NMR (300 MHz, $CDCl_3$): δ = 1.21 (6H, d, *J* = 7 Hz, CH_3CH), 4.48 (2H, m, 2 N-CH-CO), 5.11 (4H, s, 2 OCH_2Ph), 5.41 (2H, br s, 2NH), 7.2-7.40 (10 H, m, 2 Ph), ^{13}C NMR (75 MHz, $CDCl_3$): δ = 18.4, 51.7, 55.1, 67.1, 128.2, 128.3, 128.6, 136.4, 155.9, 194.

Dibenzyl[(3*R*,7*R*)-5-diazo-2,8-dimethyl-4,6-dioxononane-3,7-diyl]carbamate (11): *N*-Benzyloxycar-bonyl-*l*-valinyl diazomethane (**5**) (2.37 g, 8.6 mmol) was lithiated a according to the procedure employed for (**10**) and then treated with imidilazide (**7**) to afford the compound (**11**), purification using EtOAc: hexane as eluent furnished the pure compound (**11**) (3.15 g, 72 %) as a pale-yellow oil. Anal. calcd. $C_{27}H_{32}N_4O_6$ C 63.77, H 6.34, N 11.01 %. Found: C, 63.42; H, 6.10 ; N, 10.97 %. (KBr, ν_{max}), 3325 (NH); 2115 (CN_2); 1710 (CO_2CH_2Ph); 1632 cm^{-1} ($COCN_2$). ^1H NMR (300 MHz, $CDCl_3$): δ = 0.93-1.05 (12 H, d, *J* = 6.75Hz, $2(CH_3)_2$-CH), 2.15 (2H, m, $2CH(CH_3)_2$), 4.49 (2H, d, 2 N-CH-CO), 5.15 (4H, s, $2CH_2Ph$) 5.42 (2H, br, 2NH), 7.2-7.39 (10 H, m, 2Ph). ^{13}C NMR (75 MHz, $CDCl_3$): δ = 17.6, 19.45, 31.1, 54.6, 62.85, 67.0, 128.1, 128.2, 128.6, 136.3, 156.5.

Dibenzyl[(2*R*,6*R*)-4-diazo-3,5-dioxo-1,7-diphenylheptane-2,6-diyl]carbamate (12): *N*-Benzyloxycarbonyl-*l*-phenyl alaninyl diazomethane (2.79 g, 8.6 mmol) was converted into title compound (**12**) purification using EtOAc: hexane as eluent furnished the pure compound (**12**) (4.16 g, 80 %) as a yellow oil; anal. calcd. For $C_{35}H_{32}N_4O_6$; C, 69.52 ; H,5.34; N, 9.26 %. Found, C, 69.12; H, 5.11; N, 8.99 %. (KBr, ν_{max}), 2100 (CN_2); 1710 (CO_2CH_2Ph); 1625 cm^{-1} (COCH). ^1H NMR (300 MHz, $CDCl_3$): δ = 2.95 (4H, d, *J* = 6.85 Hz, $2CHCH_2Ph$); 4.52 (2H, m, $2CHCH_2$), 5.05 (4H, s, $2OCH_2Ph$), 5.38 (2H, m, 2NH), 7.21-7.42 (24H, s, 4 Ph). ^{13}C NMR (75 MHz, $CDCl_3$): δ = 38.25, 54.2, 58.65, 66.8, 127.1, 127.7, 128.0, 128.36, 128.36, 129.1, 135.87, 136.0,155.56, 192.54.

Synthesis of 1,3-diketones derived from amino acids: The 2-diazo-1,3-diketones in dry dichloromethane (0.01 M) was treated with rhodium(II) acetate (0.5 mol %) under nitrogen at room temperature for 1 h. The solvent was removed under *vacuo* and the remaining product was purified by preparative thin layer chromatography eluting with ethyl acetate-hexane (4:6) to yield the pure product.

Benzyl (2*R*, 6*R*)-3,5-dioxoheptane-2,6-diyldicarbamate 13: 2-diazo-1,3-diketone 10 (271.5 mg, 0.6 mmol) afforded pure 13 (217.5 mg, 85 %), (predominantly in enolic form) as an oil; Anal. calcd. $C_{23}H_{26}N_2O_6$ C 64.78, H 6.145, N 6.570 %. Found: C, 64.83; H, 6.21; N, 6.531 %. (KBr, ν_{max}) 3431 (OH enol toutomer); 3315 (NH); 1705 (CO_2CH_2); 1640 (C=O); 1618 (=COH); 1138 (C-O); 1520 cm^{-1} (Ph). δ_H ($CDCl_3$): 1.21 (6H, d, CH_3CH), 3.54 (2H,s, -$COCH_2OC$-) 4.48 (2H, m, 2N-CH-CO), 5.11 (4H, s, 2 OCH_2Ph), 5.41 (2H, br, 2NH), 7.2-7.40 (10 H, m, 2 ph), 8.41 (s,1H, -CH=), 15.4 (1 H, OH enol toutomer). ^{13}C NMR (δ/ppm, $CDCl_3$) 18.4, 65.3, 65.61, 67.1, 96.6 (CH=), 128.2, 128.3, 128.6, 136.4, 155.4, 191,191.6.

Benzyl (3*R*,7*R*)-2,8-dimethyl-4,6-dioxononane-3,7-diyldicarbamate 14: 2-Diazo-1,3-diketone **11** (305.13 mg, 0.6 mmol) afforded pure **14** (233.35 mg, 83 %) Anal. calcd. $C_{27}H_{34}N_2O_6$; C 67.20, H 7.10, N 5.80 %. Found: C, 67.187; H, 7.14; N, 5.77 %. (KBr, ν_{max}), 3431 (OH enolic toutomer); 3325 (NH); 1643 (C=O); 1618 (=COH); 1140 (C-O); 1710 cm^{-1} (CO_2CH_2Ph). δ_H ($CDCl_3$): 0.93-1.05 (12 H, d, $2(CH_3)_2$-CH), 2.15 (2H, m, $2CH(CH_3)_2$), 3.54 (2H, s, -$COCH_2OC$-), 4.49 (2H, d, 2N-CH-CO), 5.15 (4H, s, $2CH_2Ph$) 5.42 (2H, br, 2NH), 7.2-7.39 (10 H, m, 2Ph), 15.7 (1 H, OH enol toutomer), 8.38 (s, 1H, -CH=). ^{13}C NMR (δ/ppm, $CDCl_3$) 17.6, 19.45, 31.1, 65.63, 66.50, 67.0, 96.3 (CH=), 128.1, 128.2, 128.6, 136.3, 156.5, 192.9, 193.1.

Benzyl (2*R*,6*R*)-3,5-dioxo-1,7-diphenylheptane-2,6-diyldicarbamate 15: 2-Diazo-1,3-diketone **12** (362.78 mg, 0.6 mmol) afforded pure 15 (281.23 mg, 81 %) Anal. calcd. For $C_{35}H_{34}N_2O_6$; C 72.65; H 5.923; N 4.84 %. Found: C, 72.61; H, 5.89; N, 4.87 %. (KBr, ν_{max}), 3431 (OH enol toutomer); 1710 (CO_2CH_2Ph) 3318 (NH); 1625 (COCH); 1638 (C=O); 1620 (=COH) 1142 cm^{-1} (C-O). δ_H ($CDCl_3$): 2.95 (4H, d, $2CHCH_2$); 4.52 (2H, m, $2CHCH_2$), 5.05 (4H, s, CH_2Ph), 5.38 (2H, m, 2NH), 7.21-7.42 (24H, s, 4Ph), 15.9 (1 H, OH enol toutomer) 8.40 (s,1H, -CH=). ^{13}C NMR (δ/ppm, $CDCl_3$) 38.25, 65.63, 67.6, 66.8, 96.5(CH=), 127.1, 127.7, 128.0, 128.36, 128.36, 129.1, 135.87, 136.0,155.56, 192.84, 193.

General procedure for preparation of transition metal complexes (16a-18c): A mixture of 5 mmol of ligands **13**, **14** and **15** and 2.5 mmol of appropriate transition metal acetate [Ni(II), Cu(II), zinc(II)] and 50 mL of anhydrous ethanol was stirred at 50-60 ºC for 3 h. The coloured solid complex obtained was washed with ethanol and then with ethyl acetate. The yield was obtained in 74-79 %. The corresponding metal complexes were crystallized by dichloromethane.

***Bis*-(β-diketonato) Cu(II) complexes 16a, 17a and 18a:** Pale green crystals of Cu(II) β-diketonate **16a** Yield: 76 %. Anal. calcd. For $C_{46}H_{50}N_4O_{12}Cu$: C 60.42; H 5.52; N 6.124; Cu 6.95 %. Found: C, 60.35; H, 5.45; N, 6.021; Cu, 6.87 %. (KBr, ν_{max}) 1623 (C=O); 1118 cm^{-1} (C-O). δ_H ($CDCl_3$): 8.78 (s,2H, -CH=). ^{13}C NMR (δ/ppm, $CDCl_3$) 96.87, 191,191.6.

Similarly, the complexes **17a** and **18a** were prepared by the same method. Cu(II) β-diketonate **17a** Yield: 77 %. Anal. calcd. For $C_{54}H_{66}N_4O_{12}Cu$: C 63.173; H 6.48; N 5.455; Cu 6.12 %. Found: C 63.02; H 6.32; N 5.29; Cu 5.95 %. (KBr, ν_{max}), 1619 (C=O); 1120 cm^{-1} (C-O. δ_H (CDCl3): 8.38 (s,2H, -CH=). ^{13}C NMR (δ/ppm, $CDCl_3$): 96.91 (CH=), 193.2, 193.7.

Cu(II) β-diketonate **18a** yield: 79 %. Anal. calcd. for $C_{70}H_{66}N_4O_{12}Cu$: C 68.98; H 5.459; N 4.595; Cu 5.214 %. Found: C 68.87; H 5.395; N 4.487; Cu 5.00 %. (KBr, ν_{max}) 1618 (C=O); 1122 cm^{-1} (C-O). δ_H ($CDCl_3$): 8.75 (s, 2H, -CH=). ^{13}C NMR (δ/ppm, $CDCl_3$): 96.71 (CH=), 193.34, 193.76.

***Bis*-(β-diketonato) Ni(II) complexes 16b, 17b and 18b:** Green crystals of Ni(II) β-diketonate **16b** yield: 78 %. Anal. calcd. For $C_{46}H_{54}N_4O_{14}Ni$: C 58.425; H 5.76; N 5.92; Ni 6.21 %. Found: C, 58.150; H, 5.68; N, 5.86; Ni 5.98 %. (KBr, ν_{max}) 1621 (C=O); 1121 cm^{-1} (C-O). δ_H ($CDCl_3$): 8.80 (s, 2H, -CH=). ^{13}C NMR (δ/ppm, $CDCl_3$) 96.89, 191.2,191.7.

Similarly, the complexes **17b** and **18b** were prepared by the same method. Ni(II) β-diketonate **17b** yield: 79 %. Anal. calcd. For $C_{54}H_{70}N_4O_{14}Ni$: C 61.31; H 6.67; N 5.294; Ni 5.55 %. Found: C 61.01; H 6.53; N 5.220; Ni 5.43 %. (KBr, ν_{max}), 1623 (C=O); 1121 cm^{-1} (C-O. δ_H ($CDCl_3$): 8.40 (s, 2H, -CH=). ^{13}C NMR (δ/ppm, $CDCl_3$): 96.93 (CH=), 193.42, 193.79.

Ni(II) β-diketonate **18b** Yield: 78 %. Anal. calcd. for $C_{70}H_{70}N_4O_{14}Ni$: C 67.26; H 5.645; N 4.48; Ni 4.70 %. Found: C 67.02; H 5.56 N 4.37; Ni 4.41%. (KBr, ν_{max}) 1617 (C=O); 1119 cm^{-1} (C-O). δ_H ($CDCl_3$): 8.79 (s,2H, -CH=). ^{13}C NMR (δ /ppm, $CDCl_3$): 96.82 (CH=), 193.42, 194.16.

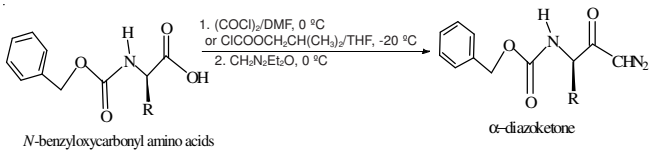
***Bis*-(β-diketonato) Zn(II) complexes 16c, 17c and 18c:** White crystals of Zn(II) β-diketonate **16c** yield: 76 %. Anal. calcd. for $C_{46}H_{50}N_4O_{12}Zn$: C 60.30; H 5.50; N 6.11; Zn 7.13 %. Found: C, 60.12; H, 5.42; N, 5.97; Zn 6.98 %. (KBr, ν_{max}) 1624 C=O); 1123 cm^{-1} (C-O). δ_H ($CDCl_3$): 8.82 (s, 2H, -CH=). ^{13}C NMR (δ/ppm, $CDCl_3$) 96.9, 191.41, 191.74.

Similarly, the complexes **17c** and **18c** were prepared by the same method. Zn(II) β-diketonate **17c** yield: 75 %. Anal. calcd. For $C_{54}H_{66}N_4O_{12}Zn$: C 63.06; H 6.47; N 5.45; Zn 6.36 %. Found: C 62.92; H 6.35; N 5.32; Zn 6.301 %. (KBr, ν_{max}), 1622 (C=O); 1118 cm^{-1} (C-O. δ_H ($CDCl_3$): 8.46 (s,2H, -CH=). ^{13}C NMR (δ/ppm, $CDCl_3$): 96.95 (CH=), 193.51, 193.82.

Zn(II) β-diketonate **18c** yield: 74 %. Anal. calcd. for $C_{70}H_{66}N_4O_{12}Zn$: C 68.88; H 5.45; N 4.59; Zn 5.36 %. Found: C 68.65; H 5.34 N 4.46; Zn 5.22 %. (KBr, ν_{max}) 1622 (C=O); 1120 cm^{-1} (C-O). δ_H ($CDCl_3$): 8.82 (s, 2H, -CH=). ^{13}C NMR (δ/ppm, $CDCl_3$): 96.86 (CH=), 193.52, 194.23.

RESULTS AND DISCUSSION

N-protected amino acids were converted into α-diazoketones *via* acid chloride or mixed anhydride by treatment with ethereal diazomethane (**Scheme-I**) and after purification by chromatography gives good yield (Table-1). These *N*-protected amino acids were converted into imidazolide by treatment with 1,1'-carbonyldiimidazole (CDI) in THF solvent (**Scheme-II**).



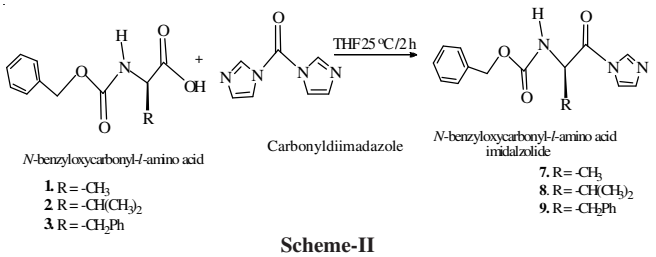
1. R = $-CH_3$
2. R = $-CH(CH_3)_2$
3. R = $-CH_2Ph$

4. R = $-CH_3$
5. R = $-CH(CH_3)_2$
6. R = $-CH_2Ph$

Scheme-I

TABLE-1
α-DIAZOKETONE DERIVED FROM *N*-PROTECTED AMINO ACID

α–Ddiazo ketone	Yield (%)
4	84
5	75
6	88



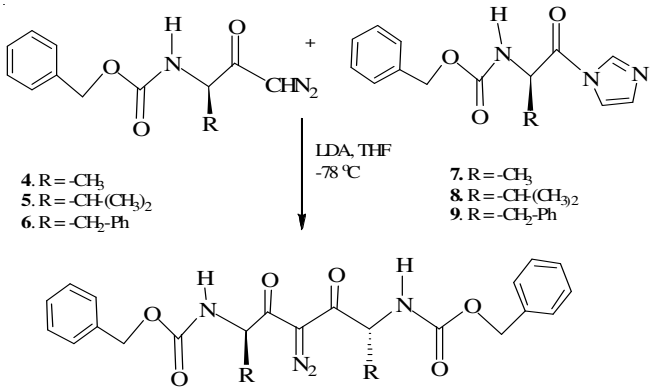
1. R = $-CH_3$
2. R = $-CH(CH_3)_2$
3. R = $-CH_2Ph$

7. R = $-CH_3$
8. R = $-CH(CH_3)_2$
9. R = $-CH_2Ph$

Scheme-II

The *N*-protected amino acid- derived diazoketone could be easily metallated by addition to a solution of lithium diisopropylamine in THF at -78 ºC. The resulting solution was treated with imidazolide to form the diazo-β-diketone (**Scheme-III**) and after the treatment of the products with aqueous work-up it is purified by chromatography to get a good yield Table-2.

Di(*N*-protected-α-amino)-2-diazo-1,3-diketones was treated with rhodium acetate to form di(*N*-protected-α-amino)-1,3-diketones (**Scheme-IV**) and after purified by chromatography to get yield (Table-3).

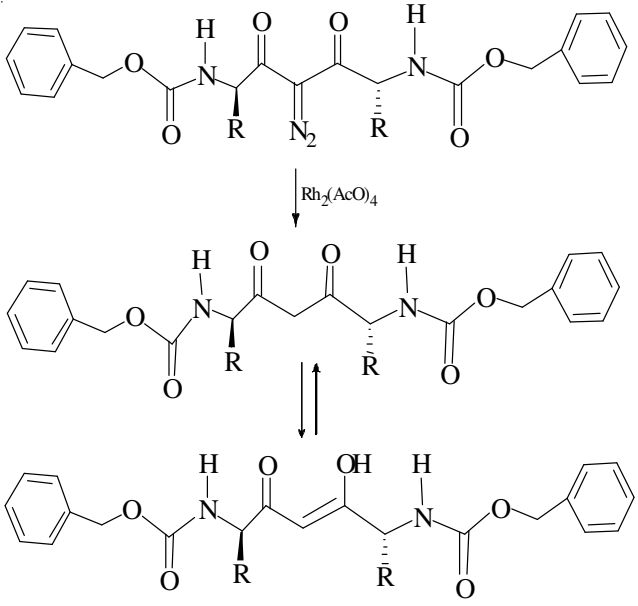


4. R = $-CH_3$
5. R = $-CH-(CH_3)_2$
6. R = $-CH_2-Ph$

7. R = $-CH_3$
8. R = $-CH-(CH_3)_2$
9. R = $-CH_2-Ph$

10. R = $-CH_3$
11. R = $-CH(CH_3)_2$
12. R = $-CH_2Ph$

Scheme-III



13. R = $-CH_3$
14. R = $-CH(CH_3)_2$
15. R = $-CH_2Ph$

Scheme-IV

TABLE-2
DIAZO-β-DIKETONES

Di(*N*-protected-α-amino)-2-diazo-1,3-diketones	Yield (%)
10	77
11	72
12	80

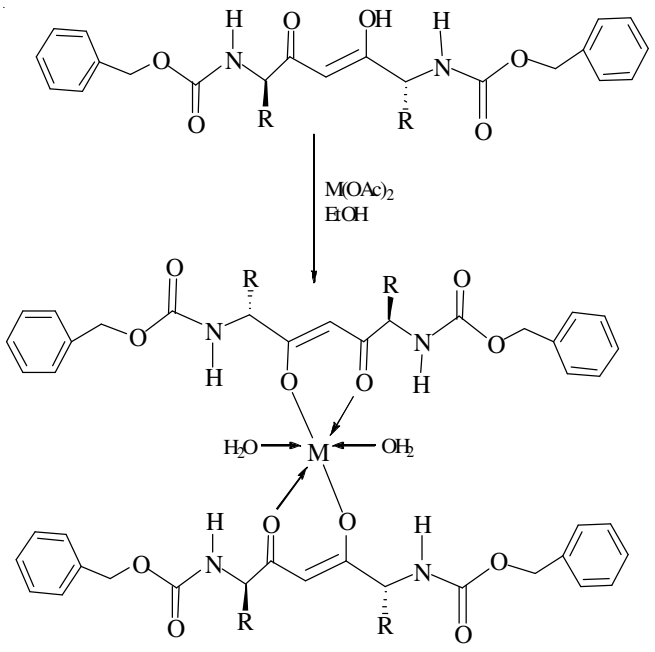
TABLE-3
β-DIKETONES

Di(*N*-protected-α-amino)-1,3-diketones	Yield (%)
13	85
14	83
15	81

Di(*N*-protected-α-amino)-1,3-diketones were used as aligands to synthesis complexes with Cu(II), Ni(II) and Zn(II) metal ions (**Scheme-V**) and after purified give good yields (Table-4).

TABLE-4
β-DIKETONES COMPLEXES

Complex	Yield (%)
16a	76
16b	78
16c	76
17a	77
17b	79
17c	75
18a	79
18b	78
18c	74



16a. R = -CH_3, M = Cu(II) **16b**. R = -CH_3, M = Ni(II)
17a. R = -$CH(CH_3)_2$, M = Cu(II) **17b**. R = -$CH(CH_3)_2$, M = Ni(II)
18a. R = -CH_2Ph, M = Cu(II) **18b**. R = -CH_2Ph, M = Ni(II)

16c. R = -CH_3, M = Zn(II)
17c. R = -$CH(CH_3)_{29}$, M = Zn(II)
18c. R = -CH_2Ph, M = Zn(II)

Scheme-V

All the synthesized transition metal complexes (**16a- 18c**) were soluble in dichloromethane, ethylacetate, acetone and methanol. The metal complexes were obtained by stoichiometric reaction of the corresponding ligand with the transition metal salt in a molar ratio M: L of 1:2. All the complexes were found to be thermally stable. Physical measurements and analytical data of the transition complexes (**16a-18c**) are given in experimental section.

Spectroscopic characterization of ligands (13-15) and their transition metal complexes (16a-18c): The complexes of synthesized compounds **13**, **14** and **15** gives green coloured Cu(II) β-diketonate **16a**, **17a** and **18a** in high yield. The structures were then confirmed by the spectral analysis: IR (KBr), ^1H and ^{13}C NMR. The C=O band in complexes **16a**, **17a** and **18a** shifted to lower frequency as compared to that of free ligand which indicates the coordination of metal atom with the carbonyl group of diketone. Similarly, other transition metal complexes were prepared by the same method.

IR spectra: The characteristic infrared spectral assignment of ligands (**13-15**) and their Ni(II), Cu(II) and Zinc(II) complexes are reported. The appearance of a strong band at 1640 cm^{-1} in the spectra of ligand is assigned to carbonyl group (C=O) and 1140 cm^{-1} due to (C-O) stretch, exhibited a lower shift of 10-20 cm^{-1} (1628-1620 and 1130-1118 cm^{-1}) in metal complexes (**16a-18c**). This shift indicates that the β-diketo functionality in ligands (**13-15**) coordinated with the transition metal ion. All the above evidences were further supported by the emergence of new bands at 535-523 and 460-443 cm^{-1} due to metal-oxygen vibrations. These new bands were only observed in the spectra of the transition metal complexes and not in their free ligands. As a conclusion, comparison of the spectra of the ligands (**13-15**) and their metal complexes (**16a-18c**) confirmed the coordination of ligand with the corresponding metal ion, bidentately through β-diketo functionality.

^1H NMR spectra: The ^1H NMR spectral data of the ligands (**13-15**) and their transition metal complexes (**16a-18c**) are provided in the experimental part. The displayed signals of all the protons of free ligands due to aromatic groups were found as to be in their expected region. The ^1H NMR spectrum of ligands (**13-15**) exhibited a singlet at δ 14.42 ppm due to enolic proton, a singlet at δ 8.41 ppm (s,1H, -CH=). The coordination of the β-diketo functionality is assigned by the down field shifting of the (-CH=,) from δ 8.40 ppm in free ligand to δ 8.77-8.86 ppm in its transition metal complexes. The enolic proton at δ 14.42 ppm in the ligand (**13-15**) disappeared in the spectra of all its metal complexes (**16a-18c**) indicating deprotonation and coordination of the oxygen with the metal ion. All other protons underwent down field shift by 0.15-0.30 ppm due to the increased conjugation on complexation with the transition metal atom.

^{13}C NMR spectra: The ^{13}C NMR spectra of the free ligands and their transition metal chelates were done in $CHCl_3$. The ^{13}C NMR spectral data are reported along with their possible assignments in the experimental section and all the carbons were found in the expected regions. The carbonyl carbon (C=O) and enolic carbon (C-O) of the ligand (**13-15**) appeared in the region δ 191-192.8 ppm and δ 191.6-193.1 ppm, respectively. The methine linkage appeared in the region δ 65.3-66.5 ppm. Downfield shifting of the carbonyl carbon (C=O)

and enolic carbon (C-O) from δ 191-192.8 ppm and δ 191.6-193.1 ppm in the free ligand (13-15) to δ 192.2-194.1 ppm and δ 192.4-194.4 ppm in its metal (II) complexes (**16a-18c**) confirmed coordination of the carbonyl (C=O) and enolic group (C-OH) to the transition metal atom. Furthermore, the presence of the number of carbons agrees well with their expected values.

Conductance and magnetic susceptibility of Ni(II), Cu(II) and Zn(II) complexes: The molar conductance values were obtained in Ω^{-1} cm^2 mol^{-1} at room temperature using DMF as a solvent (Table-5). The complexes (**16a-18c**), showed their molar conductance values in the ranges 14.6-16.8 Ω^{-1} cm^2 mol^{-1} indicating their non-electrolytic nature.

The Ni(II) complexes are paramagnetic, which indicates a high-spin-state Ni center characteristic of octahedral complexes of Ni(II). The Cu(II) complexes are paramagnetic. For the Cu(II) complexes, the μ_{eff} values are in the range 1.82-1.91 B.M., which are slightly higher than those expected for a d^9 system (1.73 B.M.) and may be due to the incomplete quenching of orbital contribution to the magnetic moment or due to spin-orbit coupling. The room temperature magnetic moment values of Zn(II) complexes are found to be diamagnetic as expected due to non-availability of unpaired electrons.

Thermogravimetric analysis: All thermal analyses were done on Perkin Elmer SII, Diamond TG/DTA thermogravimetric analyzer at VNIT, Nagpur. The thermogravimetric curves of the synthesized complexes were recorded between 300-1000 ºC in air as medium.

TABLE-5
CONDUCTIVITY AND MAGNETIC DATA OF METAL(II) COMPLEXES (**16a-18c**)

Metal complexes	Ω_M (Ω^{-1} cm^2 mol^{-1})	BM (μ_{eff}) (obs) (calc.)
16a	15.7	1.82 (1.93)
16b	16.8	3.10 (2.83)
16c	14.9	Dia
17a	15.4	1.89 (1.93)
17b	16.6	2.86 (2.83)
17c	14.6	Dia
18a	15.5	1.91 (1.93)
18b	16.7	2.95 (2.83)
18c	14.7	Dia

The TGA curves of all the complexes are almost similar and indicate a continuous weight loss till a stable metal oxide is formed. Weight loss of 3.10-4.16 % between 150-180 ºC has been observed for Nickel complex which indicate the presence of two molecules of water of coordination. On further increasing the temperature, no weight loss takes place probably due to the formation of stable metal oxides (Table-6).

TABLE-6
THERMAL DATA OF THE COMPLEXES

Complex number	Complex formula	Coordination water (%) obs (calc.)	Decom-position temp. (ºC)	Weight loss (%) obs(calc)	Residue comp.
16a	$C_{46}H_{50}N_4O_{12}Cu$	-	355	91.3	CuO
17a	$C_{54}H_{66}N_4O_{12}Cu$	-	405	92.25	CuO
18a	$C_{70}H_{66}N_4O_{12}Cu$	-	412	93.47	CuO
16b	$C_{46}H_{54}N_4O_{14}Ni$	4.16 (3.81)	334	92.1	NiO
17b	$C_{54}H_{70}N_4O_{14}Ni$	3.23 (3.41)	342	92.94	NiO
18b	$C_{70}H_{70}N_4O_{14}Ni$	3.10 (2.88)	358	94.024	NiO
16c	$C_{46}H_{50}N_4O_{12}Zn$	-	418	91.12	ZnO
17c	$C_{54}H_{66}N_4O_{12}Zn$	-	464	92.09	ZnO
18c	$C_{70}H_{66}N_4O_{12}Zn$	-	459	93.33	ZnO

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