Kinetics of the Reaction of Arylethanediylidene-bis-dithiocarbazonoate Ni Complexes with Morpholine in Benzene: Substituent and Temperature Effects

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ABSTRACT: [1-Arylethanediylidene-bis(methyl dithiocarbazonoate) NN′SS′ (−2)]Ni(II) complexes were prepared by condensation of arylglyoxals with methyl dithiocarbazoate to give the corresponding hydrazonoates. The chelation of nickel(II) with these hydrazonoates gave square planar Ni complexes. The k_3 values for the substitution of —SCH_3 close to the aryl group with morpholine (Mo) in benzene were found to increase steadily (20–35°C) followed by a sudden drop after 35°C. A continuous decrease in k_3 values was observed by further elevation in the temperature. The Arrhenius plot showed a convex curve at the whole temperatures 20–55°C, and negative $\Delta H^{\#}$ values for the reactions were obtained at 40–55°C. The Hammett plots at the temperature ranges 20–35° and 40–55°C exhibited good straight lines with ρ values of 1.44–0.73 and 1.18–1.25, respectively. The proposed mechanism is a nucleophilic aromatic substitution-like, in which the rate-determining step is the proton transfer process in the temperature range 20–35°C whereas the mechanism in the range 40–55°C passes through the attack of Mo on the carbon carrying the SCH_3 group followed by the addition of the second Mo molecule on Ni to form an intermediate, which undergoes elimination of Mo and CH_3SH to give a monosubstitution complex. © 2011 Wiley Periodicals, Inc. Int J Chem Kinet 44: 27–40, 2012

INTRODUCTION

The metal complexes synthesized by chelating of transition and nontransition metals with dithiocarbazonate derivatives have received much attention for the

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following reasons: First, they provide an interesting series of compounds, whose properties can be greatly modified by introducing different organic substituents, thereby causing a variation in the ultimate donor properties. Second, the interaction of these donors with metal ions gave complexes of different geometries and properties [1–6]. Third, these complexes are known to have some biological activity [7–9]. Fourth, these types of complexes underwent transmetalation [10–12], ligand substitution [13,14], displacement of ligand from a substrate M-L (where L is a ligand) [15], or displacement of a leaving group from the ligand complex by various reagents [16]. The reactions of some α-diketones and α-keto aldehydes with methyl dithiocarbazoate to give the corresponding mono- and bishydrazones were also reported. [3,16,17]. The series of Zn(II), Cd(II), Ni(II), Cu(II), and Pd(II) complexes of these hydrazones was obtained from the reaction of monohydrazones and bishydrazones with the corresponding metal(II) acetate or chloride [3,17]. Nickel(II) was found to form many complexes with octahedral, square planar, and tetrahedral geometries, as well as a number of five-coordinate compounds [18]. The magnetic moments of Ni complexes are temperature dependent, and equilibrium occurred between their dia- and paramagnetic forms [19,20].

The present work characterizes the nickel(II) complexes derived from arylglyoxals and methyl dithiocarbazoate, as well as their monosubstitution complexes obtained by their reactions with morpholine (Mo) in benzene. In continuation in the field of nucleophilic substitution reactions [21], the study suggests a plausible mechanism for the title reaction and discusses the effects of substituent and temperature.

EXPERIMENTAL

Solution UV spectra and kinetic measurements were recorded on a Shimadzu 160 A spectrophotometer in conjunction with a thermo-bath (TB-85) temperature control ($\pm$0.2). The infrared (IR) spectra were obtained using a FTIR-8400S Fourier transform infrared spectrophotometer (Shimadzu, Japan) using potassium bromide pellets. ^{1}H NMR spectra were carried out on a Bruker 500-MHz spectrophotometer. Nickel analyses were carried out in our laboratory by the standard method, and the results were checked by further measurements using an atomic absorption technique. The elemental analyses of the reaction products were carried out in the Microanalytical Laboratories at Cairo National Research Center (Cairo, Egypt). Magnetic susceptibility measurements were carried out by employing Gouy's balance using $Hg[Co(SCN)_4]$ as a calibrant. The effective magnetic moments were calculated after a diamagnetic correction for ligand's component using Pascal's constant.

Preparation of Methyl Dithiocarbazoate

This compound was prepared from methylation of ammonium dithiocarbazoate with methyl iodide [22] or with dimethyl sulfate [23].

Preparation of Arylglyoxal Monohydrate 1a–1f

General Procedure. Selenium dioxide solid (SeO_2; 11.1 g, 0.14 mol) in 50 mL dioxane and 2 mL H_2O was heated at 50–55°C and stirred until the solid was dissolved. Then, the mixture was added to an equivalent amount of acetophenone or acetophenone containing 4-NO_2, 4-Cl, 4-Br, 4-CH_3, and 4-OCH_3, and the resulting mixture was refluxed with stirring for 48 h. The solid part of the resulting suspension was separated, and the solution was concentrated under vacuum. The residue was extracted by a mixture of ethyl acetate and water. The organic layer was dried over anhydrous Na_2SO_4, concentrated and filtered, and the separated solid was crystallized from benzene–petroleum ether [24–27].

Phenyl Glyoxal Monohydrate **1a.** Yield 65.6%, mp 78–80°C, UV (DMSO) λ nm (ε, M^{-1} cm) = 247(12,640); 213 (3810) [24].

4-Methyl Phenyl Glyoxal Monohydrate **1b.** Yield 23%, mp 80–82°C; Anal. Calcd. for $C_9H_{10}O_3$: C, 65.06; H, 6.02; Found: C, 65.26; H, 5.91. UV (DMSO) λ nm (ε M^{-1} cm) = 259 (6460); 214 (5320). IR (KBr) ν (cm^{-1}) 3404, 3355 (OH); 1685 (C=O). ^{1}H NMR (DMSO-d_6), δ (ppm): 7.94–7.92 (d, 2H, $H_{2,6}$, J = 10 Hz,); 7.27–7.25 (d, 2H, $H_{3,5}$, J = 10 Hz,); 5.64 (s, 1H, CH); 6.69 (s, br, OH); 12.74 (s, br, OH).

4-Methoxy Phenyl Glyoxal Monohydrate **1c.** Yield 70%; mp 110–112°C; Anal. Calcd. for $C_9H_{10}O_6$: C, 59.34; H, 5.49; Found: C, 59.54; H, 5.20. UV (DMSO) λ nm (ε M^{-1} cm) = 283 (15,900); 222 (10,500). IR (KBr) ν (cm^{-1}) 3423 (OH); 1681 (C=O). ^{1}H NMR (DMSO-d_6), δ (ppm) 8.03–8.01 (d, 2H, $H_{2,6}$, J = 10 Hz,); 6.99–6.97 (d, 2H, $H_{3,5}$, J = 10 Hz,); 5.96 (d, 1H, CH); 3.43 (s, br, OH); 12.63 (s, br, OH) [25].

4-Chlorophenyl Glyoxal Monohydrate **1d.** Yield 64%, mp 90–92°C; Anal. Calcd. for $C_8H_7O_3Cl$: C, 51.47; H, 3.75; Found: C, 51.67; H, 3.58.UV (DMSO) λ nm (ε M^{-1} cm) = 257 (12,360); 214(7070). IR (KBr)

ν ($cm^{-1)}$: 3446, 3392 (OH); 1687 (C=O). ^{1}H NMR (DMSO-d_6), δ (ppm) : 8.06–8.041 (d, 2H, $H_{2,6}$, J = 8.5 Hz,); 7.55–7.53 (d, 2H, $H_{3,5}$, J = 8.5 Hz,); 5.90 (d, 1H, CH); 6.92 (s, br, OH); 13.09 (s, br, OH) [25].

4-Bromophenyl Glyoxal Monohydrate **1e.** Yield 40%, mp160–162°C; Anal. Calcd. for $C_8H_7O_3Br$: C, 41.55; H, 3.03; Found: C, 41.23; H, 3.52.UV (DMSO) λ nm (ε M^{-1} cm) = 260 (16,020); 214 (8900). IR (KBr) ν ($cm^{-1)}$: 3429, 3375 (OH); 1687 (C=O). ^{1}H NMR (DMSO-d_6), δ (ppm) 7.97–7.95 ppm (d, 2H, $H_{2,6}$, J = 10 Hz,); 7.83–7.81 (d, 2H, $H_{3,5}$, J = 10 Hz,); 5.59 (s, 1H, CH); 3.43 (s, br, OH); 13.17 (s, br, OH).

4-Nitrophenyl Glyoxal Monohydrate **1f.** Yield 24%, mp 128–130°C; Anal. Calcd. for $C_8H_7O_5N$: C, 48.73; H, 3.55; N, 7.1 Found: C, 48.61; H, 3.75; N, 7.3.UV (DMSO) λ nm (ε M^{-1} cm) = 266 (10,380); 213 (4640). IR (KBr) ν (cm^{-1}) 3332, 3251 (OH); 1703 (C=O); 1529, ($-NO_2$ asym), 1350 ($-NO_2$, sym). ^{1}H NMR (DMSO-d_6), δ (ppm) 8.18–8.16 (d, 2H, $H_{2,6}$, J = 10 Hz,); 7.78–7.76 (d, 2H, $H_{3,5}$, J = 10 Hz,); 6.58 (s, 1H, CH); 6.87 (s, br, OH).

Preparation of Aryl Ethandiylidene-bis(methyl dithiocarbazonoate) 2a–2f

General Procedure. A solution of arylglyoxal monohydrate **1a–1f** (0.1 mol) in absolute methanol (20 mL) was added to 2 mol of methyl dithiocarbazoate (0.2 mol) in absolute methanol (30 mL) and refluxed for 30 min. The resulting solution was left to cool, and the orange precipitate was filtered off, washed with methanol, and crystallized from methanol.

1-Phenyl-ethanediylidene-bis(methyl dithiocarbazonoate) **2a.** Yield 59%, mp 180°C; Anal. Calcd. for $C_{12}H_{12}N_4S_4$: C, 42.10; H, 3.50; N, 16.37; S, 37.42 Found: C, 42.20; H, 3.83; N, 16.44; S, 37.68. UV (DMSO) λ nm (ε M^1 cm) = 459 (10,640); 303 (17,190); 218 (11.810). IR (KBr) ν (cm^{-1}): 3204, 3164 (NH); 1434 (C=S); 1490 (C=N),^{1}H NMR (DMSO-d_6), δ (ppm): 8.01, 8.36 (s, 1H, CH, nonsymmetric); 7.46–7.33 (d, 5H, $H_{3,5,4,2,6}$); 2.54, 2.36 (s, 3H, S$-CH_3$, nonsymmetric); 14.72; 13.55 (s, 1H, NH, nonsymmetric).

1-(4-Methylphenyl)ethanediylidene-bis(methyl dithiocarbazonoate) **2b.** Yield 52%; mp 196–198, Anal. Calcd. for $C_{13}H_{14}N_4S_4$: C, 43.82; H, 3.93; N, 15.73; S, 35.95, Found: C, 43.67; H, 4.21; N, 15.95; S, 36.23.UV (DMSO) λ nm (ε M^1 cm) = 446 (14,060); 363 (16,660), 344 (20,190); 303 (21,520); 220 (13,670). IR (KBr) ν ($cm^{-1)}$: 3199, 3116 (NH); 1438 (C=S); 1504 (C=N). ^{1}H NMR (DMSO-d_6), δ (ppm): 7.12, 8.34 (s, 1H, CH; nonsymmetric); 7.87, 7.83 (d, 2H, $H_{3,5}$); 7.62, 7.61; 7.33, 7. 22 (d, 2H, $H_{2,6}$, nonsymmetric); 2.54, 2.53; 1.93, 1.92 (s, 3H, S$-CH_3$, nonsymmetric); 13.60, 13.52; 12.98, 12.17 (s, 1H, NH, nonsymmetric);.

1-(4-Methoxyphenyl)ethanediylidene-bis(methyl dithiocarbazonoate) **2c.** Yield 48%, mp 172–174°C; Anal. Calcd. for $C_{13}H_{14}N_4$ S_4O: C, 42.16; H, 3.78; N, 15.13; S, 34.59, Found: C, 42.47; H, 3.92; N, 15.51; S, 34.88. UV (DMSO) λ nm (ε M^1 cm) = 441 (5230); 368 (7380); 306 (7690); 217 (7590). IR (KBr) ν (cm^{-1}): 3178, 3093 (NH); 1450 (C=S); 1512 (C=N). ^{1}H NMR (DMSO-d_6), δ (ppm): 7.34, 8.34 (s, 1H, CH, nonsymmetric); 7.03, 7.01; 7.32, 7.28 (d, 2H, $H_{3,5}$, nonsymmetric); 7.69, 7.67; 7.55, 7.52 (d, 2H, $H_{2,6}$,); 2.55, 2.52; 1.95, 1.93 (s, 3H, S$-CH_3$, nonsymmetric); 13.48, 13.47; 11.94 (s, 1H, NH, nonsymmetric).

1-(4-Chlorophenyl)ethanediylidene-bis(methyl dithiocarbazonoate) 2d

Yield 58%, mp 170°C; Anal. Calcd. for $C_{12}H_{11}N_4S_4Cl$: C, 38.24; H, 2.92; N, 14.87; S, 33. 99, Found: C, 38.47; H, 3.23; N, 14.98; S, 34.18. UV (DMSO) λ nm (ε M^1 cm) = 465 (18,840); 360 (22,600); 309 (30,060); 218 (20,700). IR (KBr) ν (cm^{-1}): 3178, 3091 (NH); 1413 ^{1} (C=S); 1496 (C=N). ^{1}H NMR (DMSO-d_6), δ (ppm): 8.33, 7.99 (s, 1H, CH, nonsymmetric); 7.74, 7.72; 7.53, 7.51 (d, 2H, $H_{3,5}$, nonsymmetric); 7.55, 7.537.34, 7.32 (d, 2H, $H_{2,6}$, nonsymmetric); 2.53; 2.36 (s, 3H, S$-CH_3$, nonsymmetric); 13.55; 13.49 (s, 1H, NH, nonsymmetric).

1-(4-Bromophenyl)ethonediyildene-bis(methyl dithiocarbazonoate) **2e.** Yield 46.66%, mp 188; Anal. Calcd. for $C_{12}H_{11}N_4S_4Br$, C, 34.20; H, 2.61; N, 13.30; S, 30.41, Found:, C, 34.47; H, 2.72; N, 13.55; S, 30.78. UV (DMSO) λ nm (ε M^1 cm) = 456 (14,360); 360 (22,600); 311 (23,540); 217 (18,500) .IR (KBr) ν (cm^{-1}): 3159, 3097 (NH); 1438 (C=S); 1504 (C=N). ^{1}H NMR (acetone-d_6), δ (ppm) : 8.10, 7.92 (s, 1H, CH, nonsymmetric); 7.77, 7.76; 7.73, 7.70 (d, 2H, $H_{3,5}$, nonsymmetric); 7.68, 7.66; 7.43, 7.41 (d, 2H, $H_{2,6}$, nonsymmetric); 2.80; 2.43 (s, 3H, S$-CH_3$, nonsymmetric); 13.66; 12.30 (s, 1H, NH, nonsymmetric).

1-(4-Nitropheyl)ethanediylidene-bis(methyl dithiocarbazonoate) **2f.** Yield 58%, mp 180; Anal. Calcd. for $C_{12}H_{11}N_5O_2S_4$, C, 37.20; H, 2.84; N, 18.08; S, 33.07, Found: C, 37.55; H, 3.11; N, 18.37; S,

33.38.UV (DMSO) λ nm (ε M^1 cm) = 455 (14,660); 348 (23,780); 218 (18,620); 365 (23,420). IR (KBr) ν cm^{-1}): 3161, 3103 (NH); 1502 (C=S); 1583 (C=N). ^{1}H NMR (acetone-d_6), δ (ppm): 7.21, 7.34; 8.32, 8.31 (s, 1H, CH, (d, 2H, $H_{3,5}$, nonsymmetric); 8.28, 8.23; 8.21, 8.18 (d, 2H, $H_{2,6}$, nonsymmetric); 2.49, 2.46; 2.06, 2.03 (s, 3H, S—CH_3, nonsymmetric); 13.76, 13.38; 11.96, 10.14 (s, 1H, NH, nonsymmetric).

Preparation of [Arylethanediylidene-bis(methyl dithiocarbazonoate) NN′SS′ (−2)]Ni(II) Complex 3a–3f

General Procedure. A hot solution of aryl ethanediylidene-bis-methyl dithiocarbazonoate (0.2 mol) in methanol (30 mL) was treated with a hot solution of nickel(II) acetate (0.2 mol) in methanol (20 mL), and the reaction mixture was refluxed for 2 h. The isolated Ni(II) complex was filtered while hot and recrystallized from chloroform.

[1-(Phenyl)ethanediylidene-bis(methyl dithiocarbazonoate) NN′SS′ (−2)]Ni(II) Complex **3a.** Yield 85%, mp 150–152°C; Anal. Calcd. for $C_{12}H_{12}N_4S_4$ Ni, C, 36.11; H, 3.01; N, 14.04; S, 32.10; Ni, 14.72. Found: C, 36.08; H, 2.99; N, 13.89; S, 31.81; Ni, 14.55. UV ($CHCl_3$) λ nm (ε M^1 cm) = 693 (3080); 556 (2380); 456 (7420);372 (11.420); 288 (28,700); 263 (32,280). IR (KBr) ν (cm^{-1}): 1559 (C=N); 1483 (C=S) 561; (Ni—N). ^{1}H NMR ($CDCl_3$), δ (ppm): 7.86 (s, 1H, CH,); 7.62–7.25 (d, 4H, $H_{3,5}$, $H_{2,6}$); 2.57, 2.44 (s, 3H, S—CH_3).

[1-(4-Methylphenyl)ethanediylidene-bis(methyl dithiocarbazonoate) NN′SS′ (−2)]Ni(II) Complex **3b.** Yield 87.8%, mp 188–190°C; Anal. Calcd. for $C_{13}H_{14}N_4S_4$ Ni, C, 37.79; H, 3.39; N, 13.56; S, 31.01; Ni, 14.22, Found: C, 37.41; H, 3.02; N, 13.33; S, 30.98; Ni,14.08.UV ($CHCl_3$) λ nm (ε M^1 cm) = 688 (2800); 458 (5340); 384 (10,340); 263 (26,140). IR (KBr) ν (cm^{-1}): 1546 (C=N); 1604 (C=S), 551 (Ni—N). ^{1}H NMR ($CDCl_3$), δ (ppm) : 7.83 (s, 1H, CH,); 7.61, 7.53 (d, 2H, $H_{3,5}$); 7.25, 7.22 (d, 2H, $H_{2,6}$); 2.45, 2.37 (s, 3H, S—CH_3).

[1-(4-Methoxyphenyl)ethanediylidene-bis(methyl dithiocarbazonoate) NN′SS′ (−2)]Ni(II) Complex **3c.** Yield 89.2% mp 180°C; Anal. Calcd. for $C_{13}H_{14}N_4S_4O$ Ni, C, 36.38; H, 3.26; N, 13.06; S, 29.85; Ni, 13.69, Found: C, 35.98; H, 2.87; N, 12.96; S, 29.34; Ni, 13.39. UV ($CHCl_3$) λ nm (ε M^1 cm) = 689 (2600); 404 (12,040); 264 (25,140). IR (KBr) ν (cm^{-1}): 1595 (C=N); 1471 (C=S), 565 (Ni—N). ^{1}H NMR ($CDCl_3$), δ (ppm): 7.84 (s, 1H, CH,); 7.59 (br, 2H, $H_{3,5}$); 6.91(br, 2H, $H_{2,6}$); 2.58, 2.44 (s, 3H, S—CH_3).

[1-(4-Chlorophenyl)ethanediylidene-bis(methyl dithiocarbazonoate)NN′SS′ (−2)]Ni(II) Complex **3d.** Yield 97.8%, mp 230°C; Anal. Calcd. for $C_{12}H_{11}N_4S_4ClNi$, C, 33.24; H, 2.53; N, 12.92; S, 29.54; Ni, 13.55. Found: C, 32.91; H, 2.25; N, 12.61; S, 29.68; Ni, 13.42. UV ($CHCl_3$) λ nm (ε M^1 cm) = 696 (4380); 462 (8180), 376 (15,200); 293 (34,640); 261 (38,200). IR (KBr) ν (cm^{-1}): 1598 (C=N); 1377 (C=S), 590 (Ni—N).^{1}H NMR ($CDCl_3$), δ (ppm): 7.82 (s, 1H, CH,); 7.56–7.25 (d, 4H, $H_{3,5}$, $H_{2,6}$); 2.57, 2.45 (s, 3H, S—CH_3).

[1-(4-Bromophenyl)ethanediyledene-bis(methyl dithiocarbazonoate)NN′SS′(−2)]Ni(II) Complex **3e.** Yield 92.89%, mp 210–212°C; Anal. Calcd. for $C_{12}H_{11}N_4S_4Br$ Ni, C, 30.15; H, 2.30; N, 11.72; S, 26.80; Ni, 12.29. Found: C, 29.87; H, 1.99; N, 11.54; S, 26.45; Ni, 12.22. UV ($CHCl_3$) λ nm (ε M^1 cm) = 696 (4260); 462 (7980), 383 (15,160), 293 (33,600), 261 (37,460). IR (KBr) ν (cm^{-1}): 1581 (C=N); 1398 (C=S), 576(Ni—N). ^{1}H NMR ($CDCl_3$), δ (ppm): 7.84 (s, 1H, CH,); 7.25 (br, 2H, $H_{3,5}$); 7.54, 7.51(d, 2H, $H_{2,6}$); 2.59, 2.52 (s, 3H, S—CH_3).

[1-(4-Nitrophenyl)ethanediylidene-bis(methyl dithiocarbazonoate)NN′SS′(−2)]Ni(II) Complex **3f.** Yield 98%, mp 226–228°C; Anal. Calcd. for $C_{12}H_{11}N_5S_4O_2Ni$, C, 32.45; H, 2.47; N, 15.77; S, 28.84; Ni, 12.33. Found: C, 32.31; H, 2.27; N, 15.36; S, 28.54; Ni, 12.77. UV ($CHCl_3$) λ nm (ε M^1 cm) = 710 (3440); 468 (6360), 369 (19,800); 269 (26,340). IR (KBr) ν (cm^{-1}): 1591 (C=N); 1396 (C=S), 582(Ni—N). ^{1}H NMR ($CDCl_3$), δ (ppm): 7.84 (s, 1H, CH,); 8.38, 8.28 (dd, 2H, $H_{3,5}$); 7.84, 7.81 (d, 2H, $H_{2,6}$); 2.94, 2.58 (s, 3H, S—CH_3).

Preparation of [Arylethanediylidene-(S-methyl-N-morpholino methyl dithiocarbazonoate)NN′SS′ (−2)]Ni(II) Complex, 4a–4f

General Procedures. A solution of the Ni(II) complex (0.2 mol) in a smallest amount of benzene was treated with Mo (molar ratio 1:10) at room temperature. The reaction mixture was followed by thin-layer chromatography until a precipitate was formed, filtered, and crystallized from chloroform.

[1-Phenylehtanediylidene-(S-methyl-N-morpholino methyl dithiocarbazonoate)NN′SS′ (−2)]Ni (II) Complex **4a.** Yield 54%, mp 180–184°C; Anal. Calcd. for $C_{15}H_{17}N_5S_3ONi$, C, 41.12; H, 3.88; N,

15.99; S, 21.93; Ni, 13.41, Found: C, 41.43; H, 3.52; N, 15.66; S, 21.72; Ni, 13.24. UV ($CHCl_3$) λ nm (ε M^1 cm) = 644 (2760); 436 (5980); 413 (5540); 294 (22,140); 255 (28,460). IR (KBr) ν (cm^{-1}): 1548 (C═N); 1429 (C═S). ^{1}H NMR ($CDCl_3$), δ (ppm): 8.08 (s, 1H, CH,); 7.39–7.25, (d, 4H, $H_{3,5}$, $H_{2,6}$); 2.60 (s, 3H, S─CH_3); 4.68, 3.79–3.73 (s, 2H, α-CH_2; 2H, β-CH_2).

***[1-(4-Methylphenyl)ethanediylidene-(S-methyl-N-morpholinomethyldithiocarbazonoate)NN′SS′(−2)]-Ni(II) Complex* 4b.** Yield 26%, mp 196°C; Anal. Calcd. for $C_{16}H_{19}N_5S_3ONi$, C, 42.50; H, 4.20; N, 15.49; S, 21.25; Ni, 12.99, Found: C, 42.82; H, 4.42; N, 15.26; S, 21.58; Ni, 12.65. UV ($CHCl_3$) λ nm (ε M^1 cm) = 641 (3380); 436 (6900), 410 (6800); 361 (9340); 293 (27,020); 256 (32,880). IR (KBr) ν (cm^{-1}): 1550 (C═N); 1421 (C═S), 563 (Ni─N). ^{1}H NMR ($CDCl_3$), δ (ppm): 7.90 (s, 1H, CH,); 7.37–7.35, 7.52, 7.51 (d 2H, $H_{3,5}$, J = 10 Hz); 7.20–7.18 (d, 2H, $H_{2,6}$, J = 10 Hz); 2.58 (s, 3H, S─CH_3); 4.69–4.67, 3.80–3.79 (d, 2H, α-CH_2, J = 10 Hz); 3.77–3.76, 3.76–3.72 (d, 2H, β-CH_2, J = 10 Hz).

***[1-(4-Methoxyphenyl)ethanediylidene-(S-methyl-N-morpholinomethyldithiocarbazonoate)NN′SS′(−2)]-Ni(II) Complex* 4c.** Yield 80%, mp 176–178°C; Anal. Calcd. for $C_{16}H_{19}N_5S_3ONi$, C, 41.05; H, 4.20; N, 14.96; S, 20.52; Ni, 12.55, Found: C, 41.27; H,4.31; N, 14.75; S, 20.33; Ni, 12.33. UV ($CHCl_3$) λ nm (ε M^1 cm) = 643 (4200); 377 (13,640); 255 (39,040). IR (KBr) ν ($cm^{-1)}$: 1550 (C═N); 1425 (C═S), 563(Ni─N). ^{1}H NMR ($CDCl_3$), δ (ppm): 8.04 (s, 1H, CH,); 6.91, (br, 2H, $H_{3,5}$); 7.25 (d, 2H, $H_{2,6}$); 2.56 (s, 3H, S─CH_3); 3.82 (br, 4H, α-CH_2 and β-CH_2).

***[1-(4-Chlorophenyl)ethanediylidene-(S-methyl-N-morpholino methyl dithiocarbazonoate)NN′SS′(−2)]Ni(II) Complex* 4d.** Yield 22%; mp 178–180°C; Anal. Calcd. For $C_{15}H_{16}ClN_5S_3ONi$, C, 38.11; H, 3.38; N, 14.82; S, 20.33; Ni, 12.43, Found: C, 38.37; H, 3.51; N, 14.79; S, 20.13; Ni, 12.35. UV ($CHCl_3$) λ nm (ε M^1 cm) = 647 (5060); 439 (10,600); 293 (40,040); 256 (43,920). IR (KBr) ν ($cm^{-1)}$: 1542 (C═N); 1388 (C═S), 570(Ni─N) .^{1}H NMR ($CDCl_3$). δ (ppm): 7.91 (s, 1H, CH,); 7.411 (d, 2H, $H_{3,5}$, J = 10 Hz); 7.36–7.34 (d, 2H, $H_{2,6}$, J = 10 Hz); 2.58 (s, 3H, S─CH_3); 4.67–4.65, 3.81–3.80 (d, 2H, α-CH_2); 3.79–3.78, 3.73–3.72 (d, 2H, β-CH_2).

***[1-(4-Bromophenyl)ethanediyledene(S-methyl N-morpholino methyl dithiocarbazonoate NN′SS′(−2)]-Ni(II) Complex* 4e.** Yield 60%, mp 188–190°C; Anal. Calcd. for $C_{15}H_{16}BrN_5S_3ONi$, C, 34.84; H, 3.09; N, 13.55; S, 18.58; Ni, 11.36, Found: C, 34.97; H, 3.21; N, 13.25; S, 18.34; Ni, 11.26. UV ($CHCl_3$) λ nm (ε M^1 cm) = 648 (3540); 440 (7260); 358 (9280); 296 (28,660); 255 (34,520). IR (KBr) ν (cm^{-1}): 1546 (C═N); 1417 (C═S), 663(Ni─N). ^{1}H NMR ($CDCl_3$), δ (ppm): 7.94 (s, 1H, CH,); 7.52–7.50 (d 2H, $H_{3,5}$, J = 10 Hz); 7.34 (br, 2H, $H_{2,6}$); 2.58 (s, 3H, S─CH_3); 4.65 (br, 2H, α-CH_2); 3.80–3.73, (m, 6H, β-CH_2).

***[1-(4-Nitrophenyl)ethanediylidene(S-methyl-N-morpholinomethyldithiocarbazonoate)NN′SS′(−2)]Ni-(II) Complex* 4f.** Yield 44%, mp 222°C; Anal. Calcd. for $C_{15}H_{16}N_6S_3O_3Ni$, C, 37.29; H, 3.31; N, 17.40; S, 19.88; Ni, 12.16, Found: C, 37.47; H, 3.49; N, 17.55; S, 19.53; Ni, 11.92. UV ($CHCl_3$) λ nm (ε M^1 cm) = 656 (2940); 445 (6480); 359 (16,520); 262 (25,720). IR (KBr) ν (cm^{-1}): 1539 (C═N); 1404 (C═S), 559(Ni─N). ^{1}H NMR ($CDCl_3$), δ (ppm): 8.26 (s, 1H, CH,); 7.35–7.25 (d, 4H, $H_{3,5}$, $H_{2,6}$); 2.60 (s, 3H, S─CH_3); 4.66 (br, 2H, α-CH_2); 3.93–3.76, (m, 6H, β-CH_2).

Kinetic Measurements

The reaction of [1-arylethanediylidene-bis(methyl dithiocarbazonoate) NN′SS′ (−2)] nickel(II) complexes (1×10^{-4} mol dm^{-3}) with different concentrations of Mo (10×10^{-4} to -30×10^{-4}) mol dm^{-3} was followed spectrophotometrically in benzene. The kinetic runs were performed by following the disappearance of the reactant at λ = 700 nm. The recorded spectra at the end of the reaction were identical to the spectra of the corresponding authentic sample of the monomorpholino complex derivatives in the same solvent. The pseudo-first-order rate constant, k_ψ , is given by the following equation:

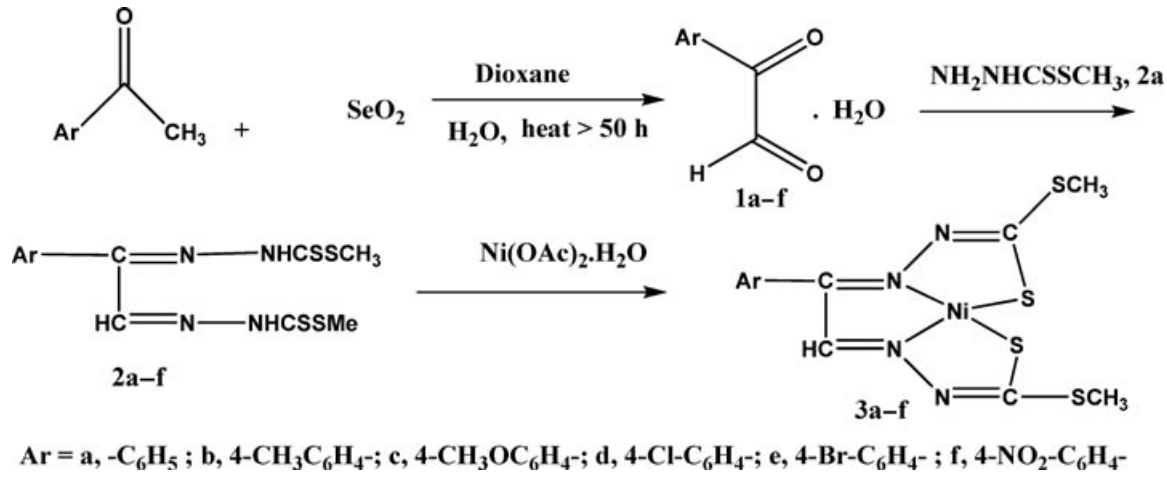
$$\log (A_t - A_\infty) = \frac{-k_\psi t}{2.303} + \log (A_o - A_\infty) \quad (1)$$

k_Ψ values were calculated from the slope of the plot of $\log (A_t - A_\infty)$ versus time (in seconds), where A_o, A_t, and A_∞ are the values of the absorbance at zero time, time t, and at the end of the reaction, respectively.

RESULTS AND DISCUSSION

Synthesis of Arylglyoxal Hydrate 1a–1f

Arylglyoxal hydrates **1a–1f** were prepared by oxidation of 4-substituted acetophenones with SeO_2 in dioxane [24,25] (Scheme 1). The FT-IR spectra of **1a–1f** revealed the presence of two broad bands at ν (cm^{-1}) 3251–3446 corresponding to two ─OH groups.



Scheme 1

^{1}H NMR confirmed the presence of two broad signals at δ (ppm) 3.43–6.92 and 12.63–13.17 attributable to two OH groups, whereas the singlet at δ (ppm) 5.59–6.58 was attributed to the =CH proton. These observations indicated that the arylglyoxals exist in the hydrated form.

Synthesis of Arylethanediylidine-bis(methyl dithiocarbazonoate) 2a–2f

The condensation of arylglyoxal hydrates **1a–1f** with methyl dithiocarbazoate yielded the bishydrazones **2a–2f** (Scheme 1). The ^{1}H NMR spectra of hydrazones **2a–2f** showed two singlets assigned to azomethine CH=N protons, two doublets of doublet for $H_{3,5}$ and $H_{2,6}$, two signals corresponding to two different S—CH_3 protons, two signals of SH protons, and other two signals in most substituent for —NH protons. These observations can be attributed to the nonsymmetric nature of the molecule rather thione → thiol tautomers [5] because the ^{1}H NMR spectra of the corresponding symmetric diacetyl and benzil bis(dithiocarbazone) do not exhibit such a behavior.

Synthesis and Geometry of Arylethanediylidene-bis(methyl dithiocarbazonoate)Nickel Complexes 3a–3f

Nickel(II) chelates of the hydrazone derivatives **3a–3f** were prepared either directly from the reaction of the ligand **2a–2f** with nickel acetate in a (1:1) molar ratio or in situ from the reaction of arylglyoxal **1a–1f** with methyl dithiocarbazonoate and nickel acetate (1:2:1 molar ratio, respectively) in ethanol (Scheme 1).

The IR frequency of the N—H band disappeared showing thereby coordination of the sulfur to the nickel(II) by the loss of the thiolic protons of the ligand. This agrees with the lack of signals due to the resonance of NH and SH protons in the ^{1}H NMR study. All isolated Ni(II) chelates **3a–3f** were found to exhibit sharp ^{1}H NMR signals indicating that they are diamagnetic, a result that infer a square planar environment around the Ni(II) ion [16,25–28]. The electronic spectra of the complexes **3a–3f** in benzene, chloroform, and Nujol mull showed intense bands at 691–742 nm (14471–13477 cm^{-1}), which should be assigned to d(M) → π*(L) transition.

The green-colored complexes **3a–3f** were found to be only feebly paramagnetic (μ = 0 → 0.55 BM at 298 K), suggesting a planar environment of ligand around the nickel(II) ion [20]. These complexes showed insignificant magnetic properties when they were measured at 55°C meaning that the complexes still have a square planar geometry on increasing temperature [20].

Synthesis of Monosubstituation Nickel(II) Complexes 4a–4f

The complexes **3a–4f** underwent either nucelophilic attack on the Ni atom or nucleophilic substitution of the —SCH_3 group or both [3,17,29]. At low concentration of amine and because the first formed monosubstituted product deactivated the other C—SCH_3 group, the momosubstituted chelates **4a–4f** were isolated. The attack of the nucleophile on the Ni atom without the release of the SCH_3 group gave a monoaddition complex **5a–5f**, whereas with the release of —SCH_3 a monoaddition monosubstitution [16] was isolated. On the other hand,

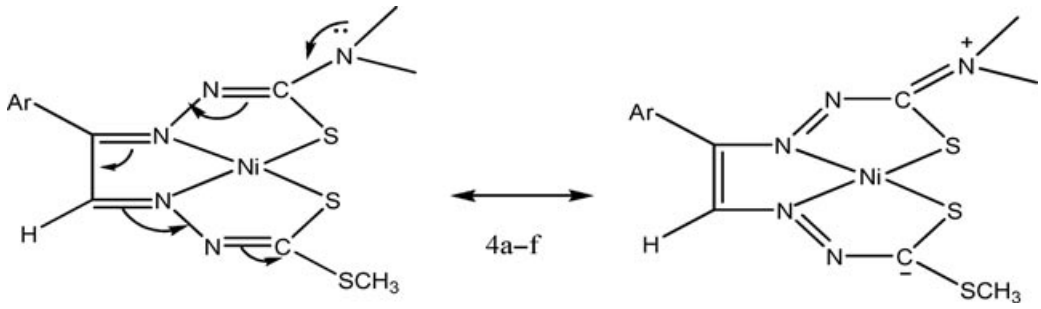


Figure 1 Delocalization of the lone pair on nitrogen of the morpholinyl group, and carbon carries the $-SCH_3$.

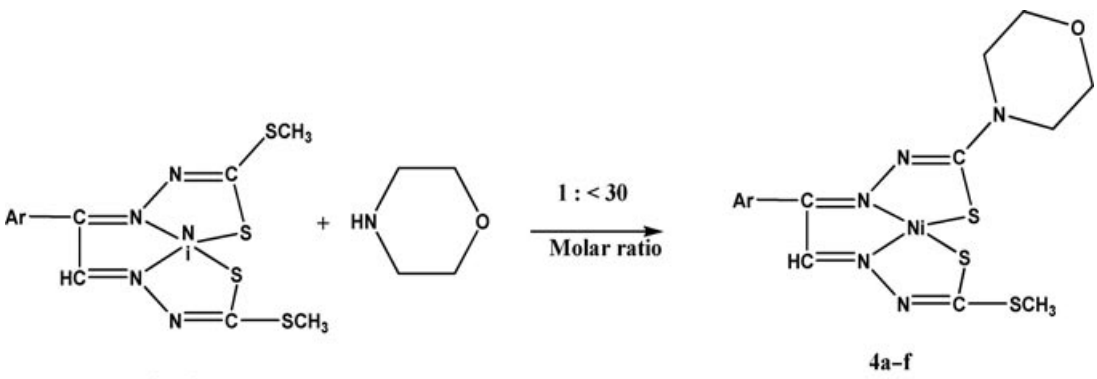
in the presence of large excess of amine, the complexes **3a–3f** gave disubstitution products [16].

In the present investigation, the reactions of [1-arylethanediylidene-bis(methyl dithiocarbazonoate) NN′SS′ (-2)]Ni(II) **3a–3f** with Mo in benzene undergo mono-morpholino-demethyl-thiolation to give the corresponding [1-arylethanediylidene (methyl morpholino dithiocarbazonoate) NN′SS′]Ni(II) complex derivatives **4a–4f**, as indicated by their elemental analysis, UV, IR, and ^{1}H NMR spectra (Eq. (2)).

carbon bearing the other $C-SCH_3$. This inhibits further attack on that carbon, and consequently no disubstitution products are obtained under these conditions of the reaction (Fig. 1).

Kinetic Studies and Mechanism for the Reaction of Arylethanediylidine-bis(methyl dithiocarbazonoate)Nickel(II) Complexes 3a–3f with Mo in Benzene

The titled reaction is considered as a bimolecular nucleophilic aromatic substitution-like, i.e., nucleophilic



Ar = a, C_6H_5; b, 4-$CH_3C_6H_4$; c, 4-$CH_3OC_6H_4$; d, 4-ClC_6H_4; e, 4-BrC_6H_4; f, 4-$NO_2C_6H_4$. (2)

The ^{1}H NMR spectral data of these complexes display only one signal at δ 2.58–2.60 ppm corresponding to only one $-SCH_3$ group and only one morpholinyl proton. The bands displayed at 651–655 (15,360–15,267 cm^{-1}) in benzene, and at 641–656 nm (15,600–15,243 cm^{-1}) in $CHCl_3$ can be attributed to $d(M) \rightarrow \pi^*(L)$ transition. The assumed square planar geometry for these complexes was confirmed from the zero value of their room temperature magnetic moment. The reason that the reaction of **3a–3f** with Mo of the concentration less than 30 folds gave only monosubstitution products **4a–4f** can be explained on the basis of the delocalization of the fourth electron on the mopholinyl nitrogen creates a negative charge on the

substitution and not ligand substitution [13]. In general, the nucleophilic substitution reactions involving amine at sp^2 carbon have been suggested to proceed through unanalyzed or amine-catalyzed mechanism or a mixture of them. The catalyzed mechanism could proceed by a dimer mechanism [30–32], specific base (SB) [33–35], or SB-general acid mechanism (SB-GA) [36]. The reaction conditions, e.g., the nature of the solvent [37,38], the nature of the amine [38,39], and the structure of the reacting species, were used to decide which mechanism was operating.

Table I Rate Constants and Activation Parameters for the Reaction of Substituted Ni(II) Complexes **(3a–3f)** with Mo in Benzene at Temperatures 20–35°C

	k_3 ($\times 10^{-2}$ dm^6 mol^{-2} s^{-1})					
R	20°C	25°C	30°C	35°C	$\Delta H^{\#}$ (kcal mol^{-1})	$-\Delta S^{\#}$ (cal mol^{-1}K^{-1})
4-NO_2	69.79	102.4	110.76	–	1.99	39.58
4-Cl	7.45	9/09	13.16	14.71	8.13	42.84
4-Br	7.18	8.77	11.69	13.89	8.15	42.94
H	4.65	5.68	7.50	9.21	8.67	43.90
4-CH_3	3.08	3.92	5.02	6.67	8.85	44.37
4-OCH_3	2.40	3.03	4.09	5.00	9.08	44.77
ρ	1.44	1.42	1.35	0.73		

Table II Rate Constants and Activation Parameters for the Reaction of Substituted Ni(II) Complexes **(3a–3f)** with Mo in Benzene at Temperatures 40–55°C

	k_3 ($\times 10^{-2}$ dm^6 mol^{-2} s^{-1})						
R	35°C	40°C	45°C	50°C	55°C	$-\Delta H^{\#}$ (kcal mol^{-1})	$-\Delta S^{\#}$ (cal mol^{-1}K^{-1})
4-NO_2	29.82	27.78	25.60	23.54	22.73	3.43	43.45
4-Cl		6.69	5.97	5.13	4.70	5.46	46.61
4-Br		6.22	5.58	4.86	4.60	5.50	46.65
H		4.36	3.80	3.33	3.00	5.68	47.48
4-CH_3		2.46	2.13	1.85	1.65	5.96	48.67
4-OCH_3		1.38	1.20	1.08	0.94	6.18	49.83
ρ		1.18	1.19	1.20	1.25		

Reactions of 3a–3f with Mo in Benzene: Effects of Substituents and Temperature

The rate of reactions of **3a–3f** with Mo obeyed the pseudo-first-order kinetics with excess Mo, and the plots of k_ψ (s^{-1})/[Mo] against the corresponding [Mo] gave a straight line passing through the origin with slopes equal to third-order rate constants, k_3 (dm^6 mol^{-2} s^{-1}), indicating that the reaction depends on two amine molecules, i.e., amine-catalyzed reaction. The third-order rate constants, the activation parameters, and ρ are presented in Tables I and II.

Interestingly, the k_3 values were found to increase steadily with increasing temperature in the range 20–35°C followed by a sudden drop after 35°C, then a continuous decrease in k_3 values was observed by further elevation of the temperature in the range 40–55°C, whereas this behavior is observed in 4-nitro derivative **3f** in the range 35–55°C (Tables I and II).

The kinetic results with temperatures ranging between 20 and 55°C show a convex curve for the Arrhenius correlation (Fig. 2). The entropies of activation were quite similar for both reactions in the temperature ranges 20–35° and 40–55°C. Although the plots of $\Delta H^{\#}$ versus $\Delta S^{\#}$ for the reactions of Mo with **3a–3f** at all temperatures 20–55°C gave scattered correlation, their plots in both ranges of temperatures 20–35° and 40–55° gave a good straight line (not shown). Surprisingly, the enthalpy of activation values for the reactions of **3a–3f** with Mo in the temperature range 40–55°C is negative and showed a small difference with change in the nature of the substituent [39] (Table II). These observations are presumably due to heat capacity changes in the activated complex, temperature-induced changes in the ground state, or a combination of both, conformational switches of the structure of the starting materials, or finally the reaction follows the same mechanism but with different positions in the rate-determining step [34].

Accordingly, Scheme 2 may be suggested to account for the isolation of the monosubstitution products **4a–4f** at 20–35°C**.** The mechanism shows that the first Mo molecule attacks the electrophilic carbon that bears the $-SCH_3$ group close to the aryl group to form the zwitterionic intermediate (I). As expected, the formation of the highly ionic intermediates (I) is not favored in nonpolar solvents, and the second Mo molecule can thus deprotonates the intermediate (I) to give an anionic intermediate (II). Finally, this intermediate undergoes decomposition to give the monosubstitution product **4a–4f** and the reaction follows the SB mechanism. Another suggested mechanism is that the protonated

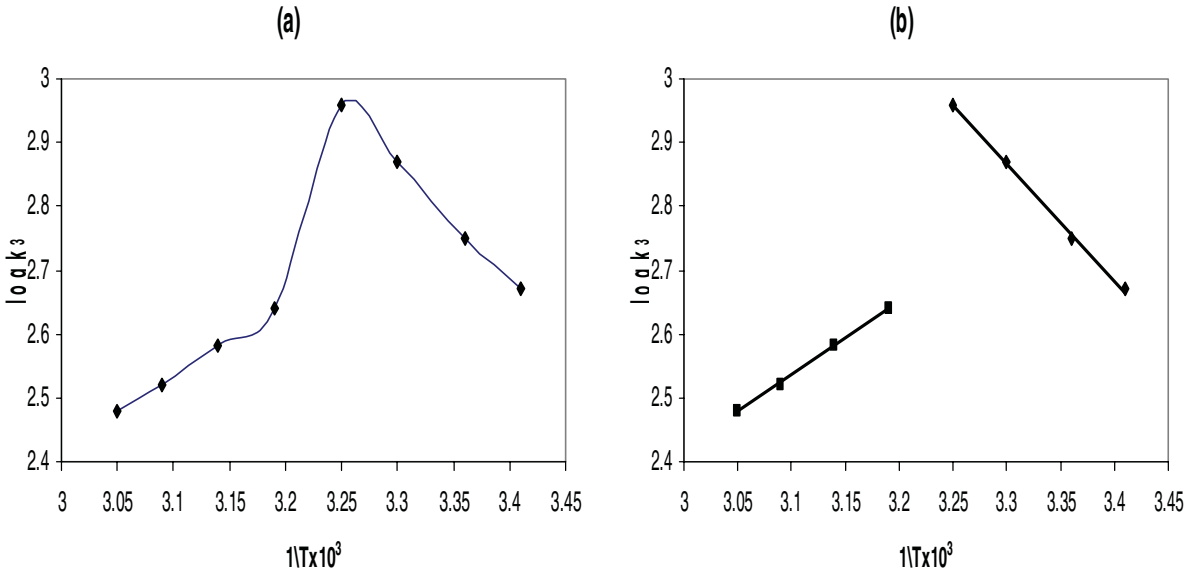


Figure 2 Plot of log k_3 versus $1/T$ for the reaction of **3a** with Mo in benzene: (a) convex and (b) two separate series 20–35°C and 40–55°C.

Mo donates a proton to the leaving $-SCH_3$ group, and the reaction follows the SB-GA mechanism. Such a mechanism cannot be applied in our reaction because it is known that this mechanism actually occurs in dipolar solvent especially DMSO [36]. Another investigation of the reaction is the dimer mechanism, where a dimer amine formed in a fast and reversible process attacks the electrophilic carbon that bears the $-SCH_3$ group close to the aryl group, and at the same time donates a proton to the leaving group, followed by the involvement of a third amine to give the final products **4a–4f**. This mechanism is also unfavorable because the correlation between k_A and [Mo] is not curvilinear [30–32]. The elimination of the uncatalyzed pathway (Scheme 2) is based on the fact that the reaction is amine catalyzed.

The kinetic expression for the reaction of **3a–3f** with Mo is derived with reference to Scheme 2, where a k_2 pathway is neglected. Making the usual assumption that the zwitterionic adduct may be treated as a steady-state intermediate when the amine acts as both the nucleophile and the catalyzing base, the overall rate constant is given by the following equation:

$$k_A = \frac{k_\psi}{[\mathrm{Am}]} = \left(\frac{k_1 k_3^{\mathrm{Am}} k_4 [\mathrm{Am}]}{k_{-1}k_4 + k_3^{\mathrm{Am}} k_4 [\mathrm{Am}] + k_{-1} k_{-3}^{\mathrm{Am}}} \right) \tag{3}$$

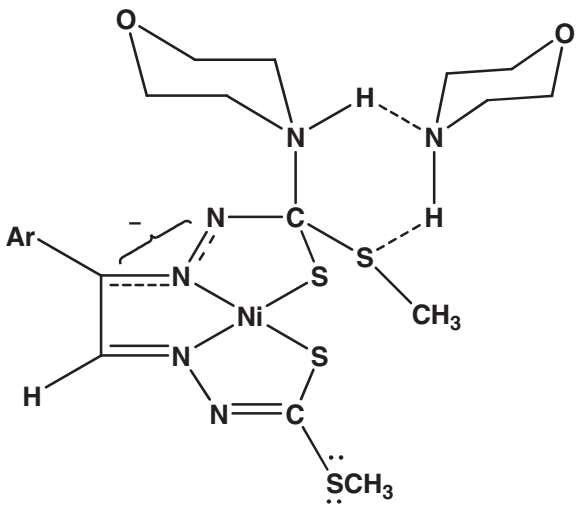
where k_Ψ is the pseudo-first-order rate constant and k_A (k_ψ (s^{-1})/[Am] is the second-order rate constant.

If we assume that k_1 is the rate-determining step, i.e., $k_{-1}k_4 + k_{-1}k_{-3}^{\mathrm{Am}} \ll k_3^{\mathrm{Am}} k_4$ [Am]

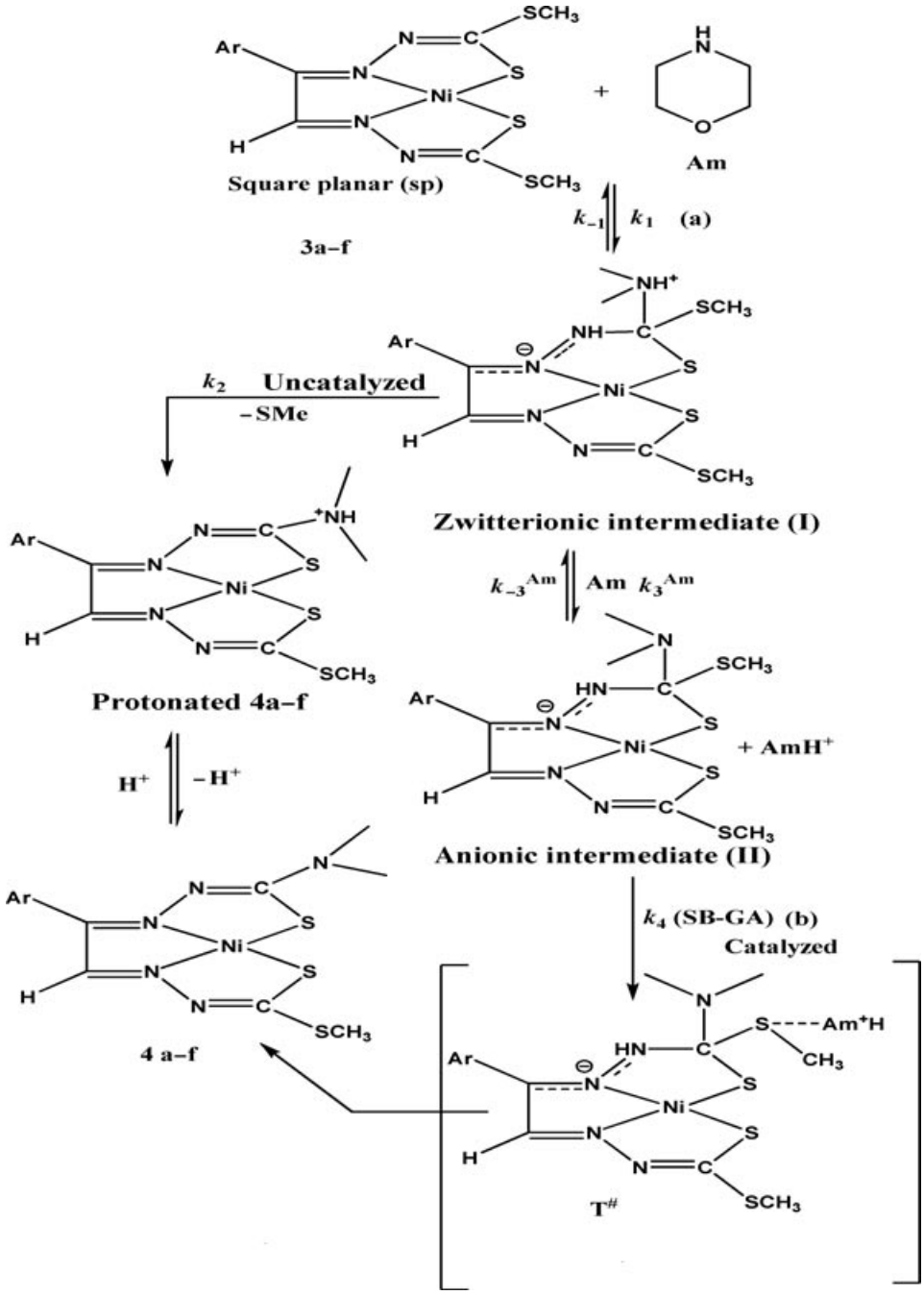
$$k_A = \frac{k_1 k_3^{\mathrm{Am}} k_4 [\mathrm{Am}]}{k_3^{\mathrm{Am}} k_{4[\mathrm{AM}]}} = k_1 \tag{4}$$

If we assume that k_3 is the rate-determining step, $k_{-1}\, k_4 \gg k_3^{\mathrm{Am}} k_4 [\mathrm{Am}] + k_{-1} k_3^{\mathrm{Am}}$

$$k_A = \frac{k_1 k_3^{\mathrm{Am}} k_4 [\mathrm{Am}]}{k_{-1} k_4} = k_3^{\mathrm{Am}} K_1 [\mathrm{Am}] \tag{5}$$



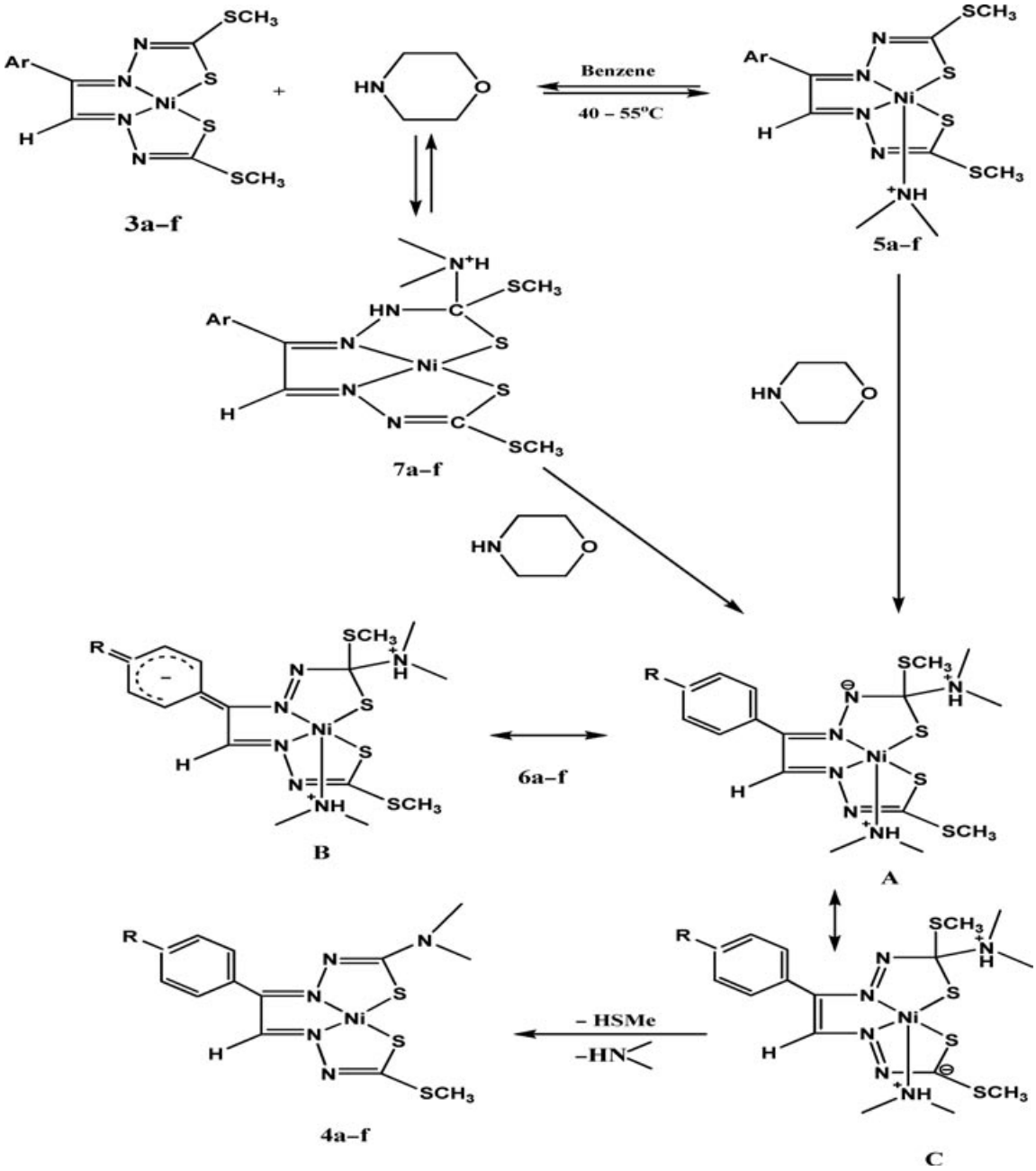
Cyclic anionic intermediate (III)



Scheme 2

Consequently, Eq. (5) is consistent with a mechanism in which the proton transfer process is the rate-determining step, i.e., SB.

An alternative mechanism for the reaction of **3a–3f** with Mo in benzene to produce monosubstitution is shown in Scheme 3. It shows that the reaction of Mo with complexes initially proceeds either by two pathways: The first one is the formation of monoadduct **5a–5f** followed by a further attack of the second Mo molecule on the C—SCH_3 carbon of the monoadduct **5a–5f** to form a zwitterionic intermediate **6a–6f** (structure A). The second pathway occurred by the attack of Mo on the carbon bearing the —SCH_3 close to the aryl ring to form the zwitterionic intermediate **7a–7f** followed by the attack of the second Mo molecule to give the same zwitterionic intermediate **6a–6f.** In this intermediate, the positive charge is located on the nitrogen atom whereas the negative charge can be



Scheme 3

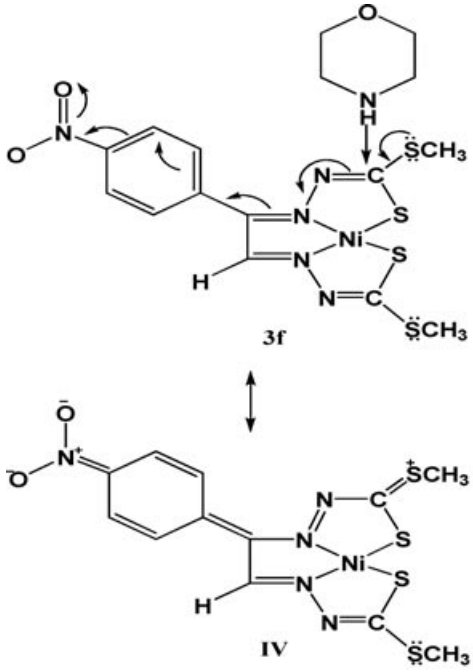
accommodated either on the aryl ring (structure B) or on the carbon atom of the other C—SCH_3 carbon through extended conjugation (structure C). Also, the electron-releasing morpholinyl group undoubtly reduces the formal positive charge on the Ni(II) ion containing intermediate **7a–7f**, thus decreasing the Ni—N bond strength. Consequently, it seems reasonable to assume that the formed monosubstituted monoadduct intermediate becomes thermodynamically less stable [16] and readily lose the axially coordinated base with accompanying elimination of the CH_3SH molecule giving rise to the monosubstitution product **4a–4f**.

Kinetics and Mechanism for the Reaction of 3a–3f with Mo in the Temperature Range between 20 and 35°C

In the preceding discussion, we suggested that the reaction of **3a–3f** with Mo in benzene proceeds by the mechanism shown in either Scheme 2 or Scheme 3. The

Hammett plots exhibited good straight lines with ρ values of 1.42–0.73, depending on temperature and r values of 0.93–0.98.

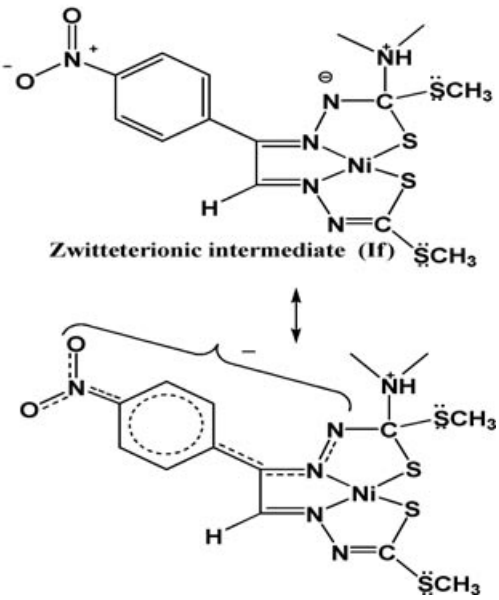
It was reported that the carbon carrying the $-SCH_3$ group close to the aromatic ring in the nickel complex **3a** possesses higher electrophilicity than the other C—SMe carbon, and thus, the nucleophilic attack of amines will preferentially occur on the former carbon [16]. On the other hand, the delocalization of the developed negative charge with the aromatic ring to give the stable zwitterionic intermediate II can explain the regioselectivity to give the monosubstitution **4a–4f**. This charge delocalization presumably gives stable zwitterionic intermediates **I**, whereas such delocalization hardly occurs with the aromatic ring if Mo attacks the $C-SCH_3$ far from the aryl group. Table I reveals that an electron-withdrawing substituent, e.g., NO_2 **3f** accelerates the rate of nucleophilic attack. We ascribed the increase in the rate to the increase in the electrophilicity of the carbon atom bearing the $-SCH_3$ group located close to the aryl group, as well as the $-NO_2$ group stabilization of the tetrahedral intermediate (**If**). Meanwhile, the resonance between the developed negative charge and the $-NO_2$ group retards the departure of the leaving group IV.



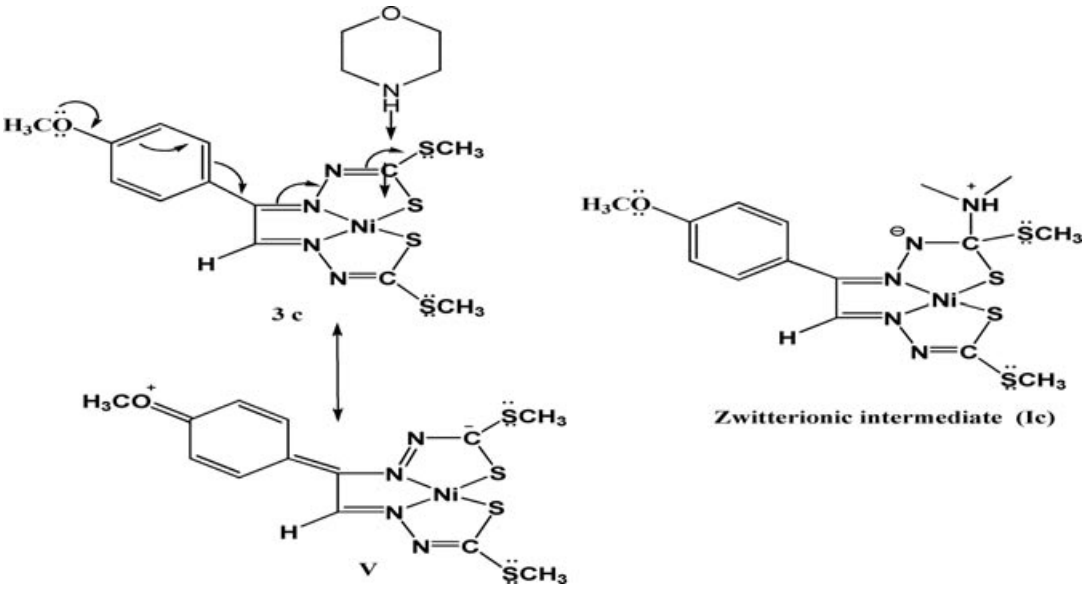
In contrast, Table I shows that an electron-donating substituent, e.g., $-OCH_3$ **3c**, inhibits the nucleophilic attack. We ascribed the decrease in the rate to the decrease in the electrophilicity of the carbon atom bearing the $-SCH_3$ group close to the aryl group due to the resonance as found in structure V, whereas at the same time the 4-OCH_3 group destabilizes **Ic** and increases the expulsion rates of the leaving group $-SCH_3$ (the k_4 value) from **Ic**. See the structure in the next section.

Kinetics and Mechanism for the Reactions of 3a–3f with Mo in the Temperature Range of 40–55°C

As mentioned previously, the k_3 values at 40°C suffer from a sudden drop followed by a continuous decrease in the k_3 value for all substituents with an increase in the temperature till 55°C. The Hammett plots exhibited a good linear correlation with ρ values ranged between 1.18 and 1.25 ($r = 0.96$–0.99; Table II). We noticed that the ρ values have a relatively small difference with the change in temperature, and unexpectedly it increased with increasing temperature. However, the calculated ρ values for the reaction with Mo in the temperature range 40–55°C are comparable to those measured for the same reactions at the temperature range 20–35°C. As a result, the effect of substituents on rates is similar to those for the reaction of **3a–3f** with Mo in the temperature range 40–55°C.



Accordingly, many mechanisms for the reactions of **3a–3f** with Mo in the temperature range 40–55°C could be interpreted based on the following: (i) the reaction in the two temperature ranges follows the SB mechanism (Scheme 2); with a change in the position of the



slow step, the rate-limiting step is the proton transfer process in the temperatures 20–35°C, whereas it may be the departure of the $-SCH_3$ group (product formation) in the temperatures 40–55°C. This is not possible because ρ values in both ranges 20–35°C and 40–55°C of temperatures are quite the same. (ii) The reaction may follow a dimer-mechanism involving intermediate (III). This mechanism is rejected on the ground that no parabolic k_A – [Am] shape was observed [30–32]. (iii) A reduction in the splitting of the 3d energy level by the ligand to produce a square-planar paramagnetic complex [20]. And (iv) the complexes **3a–3f** are subjected to a fast configurational equilibrium, which is greatly enhanced by increasing the temperature. The comparable ρ and entropy values as well as the decrease in k_3 values with increasing temperature may be consistent with the fast configurational equilibrium mechanism, where the proton transfer process is still the rate-determining step. One might conclude that the decrease in k_3 values with increasing temperature is due to the fact that the equilibrium is shifted continuously toward the square planar structure, which may react more slowly than the initial configuration structure with Mo [39].

However, the last two mechanisms are not accepted on the ground that (a) the electronic spectra of complex **3a** in benzene showed no change at 30°C and 55°C; (b) the addition of pyridine to a benzene solution of **3a** (1:20 molar ratio) at 30°C and 55°C accompanied by no change in the absorption bands characteristic of the square planar form (SP). This observation ruled out the formation of an octahedral bis-adduct; (c) the complex **3a** showed insignificant magnetic properties when it was measured at 55°C compared with that at 30°C, meaning that this complex still has a square planar geometry with increasing temperature; (d) it is observed that increasing the temperature from 30°C to 55°C for the reaction of **3a** with Mo in benzene increases the intensity of bands and shoulders in the range 500–660 nm (not shown). Points (a)–(c) ruled out the formation of mono adduct **5a–5f** and favor the formation of intermediate **6a–6f.**

Accordingly, the mechanism shown in Scheme 3 in which the probable pathway is the attack of Mo on the $C-SCH_3$ close to the aryl group followed by adding of the second Mo molecule to the Ni atom to form an zwitterionic intermediate **6a–6f** is largely consistent with the previous facts. This is corroborated on the basis that the monosubstituted monoadduct intermediate **7a–7f** is reported to be thermodynamically unstable [16] and consistent with the decrease in our k_3 values with increasing temperature. This intermediate undergoes elimination of Mo and CH_3SH to give the monosubstitution complex **4a–4f**.

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