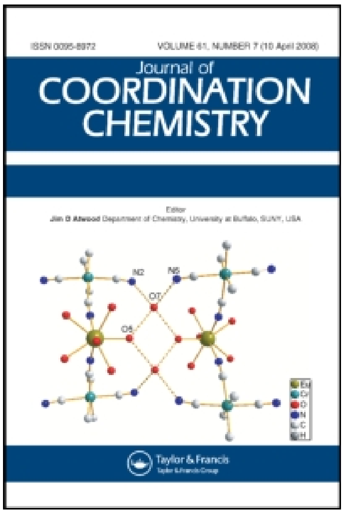

Journal of Coordination Chemistry
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713455674

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First published on: 04 September 2007

To cite this Article Şener, S. , Erçağ, A. , Şentürk, O. S. , Perpelek, E. and Sinan, F. Uğur(2008) 'Photochemical reactions of group VIB metal carbonyls with heterocyclic Schiff bases derived from 4-amino -3-hydrazino-5-mercapto-1,2,4-triazole', Journal of Coordination Chemistry, 61: 5, 740 — 749, First published on: 04 September 2007 (iFirst)

To link to this Article: DOI: 10.1080/00958970701384469

URL: http://dx.doi.org/10.1080/00958970701384469

Journal of Coordination Chemistry
Vol. 61, No. 5, 10 March 2008, 740–749

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Photochemical reactions of group VIB metal carbonyls with heterocyclic Schiff bases derived from 4-amino -3-hydrazino-5-mercapto-1,2,4-triazole

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(*Received 30 January 2007; in final form 12 March 2007*)

The new complexes, $M(CO)_5$(Schiff base) [M = Cr; **1**, Mo; **2**, W; **3**, Schiff base = 4-salicylidenamino-3-hydrazino-5-mercapto-1,2,4-triazole, SAHMT, **a**; 4-(2-hydroxynaphthylidenamino)-3-hydrazino-5-mercapto-1,2,4-triazole, 2HNAHMT, **b**; 4-(3-hydroxybenzylidenamino)-3-hydrazino-5-mercapto-1,2,4- triazole, 3HBAHMT, **c**; 4-(4-hydroxybenzylidenamino)-3-hydrazino-5-mercapto-1,2,4- triazole, 4HBAHMT, **d**; 4-(5-bromosalicylidenamino)-3-hydrazino-5-mercapto-1,2,4-triazole, 5BrSAHMT, **e**; were synthesized by photochemical reaction of metal carbonyls $M(CO)_6$ (M = Cr, Mo, W) with new heterocyclic Schiff bases derived from 4-amino-3-hydrazino-5-mercapto-1,2,4-triazole, **a**–**e**. The ligands and complexes have been characterized by elemental analysis, EI-mass spectrometry, FT-IR, ^1H and ^{13}C-{^1H}-NMR spectroscopy. The spectroscopic studies show that Schiff bases, **a**–**e**, are monodentate and coordinate *via* azomethine N donor to the central metal atom in $M(CO)_5$(Schiff base) (M = Cr, Mo, W).

Keywords: 4-Amino-3-hydrazino-5-mercapto-1,2,4-triazole; Schiff base; VIB metal carbonyls

1. Introduction

1,2,4-Triazole ligands show coordination diversity, especially when the triazole is substituted with additional donor groups [1]. These ligands have variability in binding modes owing to increased number of nitrogen atoms and attendant possibilities for isomerism [2]. A number of transition metal complexes containing 1,2,4-triazole ligands have been synthesized and characterized, usually aggregating to form dinuclear, oligonuclear and polynuclear species [1]. Metal complexes of Schiff bases derived from triazoles are biologically important ligands [3]; 1,2,4-triazoles are used to inhibit the

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Journal of Coordination Chemistry
ISSN 0095-8972 print/ISSN 1029-0389 online © 2008 Taylor & Francis
DOI: 10.1080/00958970701384469

growth of tumors and cancer in mammals [4] and to treat viral and bacterial infections [5].

Some complexes containing substituted 1,2,4-triazole ligands have spin-crossover properties and can be used as molecular-based memory devices, displays and optical switches [6, 7]. However, only a few papers have described the coordination chemistry of 1,2,4-triazole ligands with group 6 metal carbonyl complexes [8–14]; these group 6 metal carbonyl complexes with 1,2,4-triazole ligands are usually mononuclear and 1,2,4-triazole ligands exhibit η^1-bonding [15].

In this article, we prepare and characterize a series of Schiff bases, **a–e**, derived from condensation of 4-amino-3-hydrazino-5-mercapto-1,2,4-triazole with substituted hydroxy aromatic aldehydes [16] and their group 6 metal carbonyl complexes. SAHMT has been synthesized as a new corrosion inhibitor by Quraishi and Jamal [17] but spectroscopically characterized by us. Schiff base ligands **a–e** have potential coordinating sites: (1) the sulfur of the thiol or thione group, (2) the nitrogen of the azomethine group, (3) two nitrogen atoms at positions 1 and 2 in the triazole ring system, (4) the nitrogens of the hydrazine group and (5) phenolic hydroxyl group in the aldehydes. These ligands have aroused our interest in elucidating the structures of carbonyl complexes with these Schiff bases. The ligands are monodentate via azomethine nitrogen [(H–C = N) exocyclic] to the metal center atom in metal carbonyl complexes.

The synthesized ligands, **a–e**, and complexes were characterized by elemental analyses, electron impact mass spectrometry, FT-IR, ^{1}H and ^{13}C-{^{1}H}-NMR spectroscopy.

2. Experimental

2.1. *Apparatus*

Elemental analyses were carried out using a LECO-CHNS-O-9320 by Technical and Scientific Research Council of Turkey, TUBİTAK.

FTIR spectra were recorded on samples in KBr at the Ege University on a Mattson 1000 FT spectrophotometer.

^{1}H and ^{13}C-{^{1}H}-NMR spectra in DMSO were recorded on a Varian AS 400 MHz and Bruker 400 MHz Digital FT-NMR at Ege University and TUBİTAK.

Electron impact mass spectra were recorded on a Micromass VG Platform-II LC-MS at TÜBİTAK.

UV irradiations were performed with a medium-pressure 400 W mercury lamp through a quartz-walled immersion well reactor.

2.2. *Materials*

The solvents, aldehydes and silica gel were purchased from Merck, $M(CO)_6$ (M = Cr, Mo, W) and 4-amino-3-hydrazino-5-mercapto-1,2,4-triazole were purchased from Aldrich. These reagents were used as supplied.

2.3. *Preparation of Schiff bases*

The Schiff bases, **a**–**e**, were synthesized by the following typical procedure. 4-(5-bromosalicylidenamino)-3-hydrazino-5-mercapto-1,2,4-triazole, 5BrSAHMT, **e**; 4-amino-3-hydrazino-5-mercapto-1,2,4-triazole (0.1 mol) and 5-bromosalicyl aldehyde (0.1 mol) were dissolved in ethanol (100 cm^3) containing a few drops of concentrated HCl and the mixture was heated under reflux on a waterbath for ca 3–4 h. The product separated on evaporation of the alcohol and was recrystallized from EtOH in 70% yield.

2.4. *Preparation of complexes*

Reactions were carried out under dry nitrogen using Schlenk techniques. All solvents were dried and degassed prior to use.

The air stable complexes, $M(CO)_5$(Schiff base) (M = Cr (**1**), Mo (**2**), W (**3**), were prepared by photochemical reactions of metal carbonyls $M(CO)_6$ (M = Cr, Mo, W), with Schiff bases SAHMT, **a**; 2HNAHMT, **b**; 3HBAHMT, **c**; 4HBAHMT, **d**; 5BrSAHMT, **e** in 70–80% yields by methods of which the following is typical.

$Cr(CO)_6$ (0.22 g, 1 mmol) and SAHMT, **a** (0.12 g, 0.5 mmol) were dissolved in tetrahydrofuran (80 mL). The solution was irradiated for 1 h using a 400 W medium pressure mercury lamp through a quartz-walled immersion well reactor while stirring at −78°C in ice-acetone mixture. During the irradiation, the color changed from colorless to yellow. After irradiation, the reaction mixture was evaporated under vacuum, yielding a light yellow solid. The solid was then filtered, washed with alcohol and hexane and dried under vacuum. Yield of [$Cr(CO)_5$(SAHMT)]: 79%.

3. Results and discussion

The photogeneration of $M(CO)_5$ from $M(CO)_6$ (M = Cr, Mo or W) has been extensively studied. These 16-electron $M(CO)_5$ fragments react with any available donor to form $M(CO)_5L$ species, and where L is a chelating bidentate ligand, rapid continuation to the chelating $M(CO)_4L$ or bridging $M_2(CO)_{10}(\mu\text{-}L)$ products may occur [18–20]. In this study, the Schiff base ligands and complexes [$M(CO)_5$(Schiff base)] (M = Cr (**1**), Mo (**2**), W (**3**)); Schiff base; SB = **a**–**e**, (**1a**)–(**3a**), (**1b**)–(**3b**), (**1c**)–(**3c**), (**1d**)–(**3d**) and (**1e**)–(**3e**) were prepared by the photochemical reaction of $M(CO)_6$ with **a**–**e**. The spectroscopic studies show that **a**–**e** are monodentate, coordinating via azomethine nitrogen [(H–C=N) exocyclic] in the complexes. Analytical data of **a**, (**1a**)–(**3a**), **b**, (**1b**)–(**3b**), **c**, (**1c**)–(**3c**), **d**, (**1d**)–(**3d**) and **e**, (**1e**)–(**3e**) are given in table 1.

Selected infrared spectral data of **a**–**e**, (**1a**)–(**3a**), (**1b**)–(**3b**), (**1c**)–(**3c**), (**1d**)–(**3d**) and (**1e**)–(**3e**) are presented in table 2.

Based on earlier work [16, 21] on 4-amino-3-hydrazino-5-mercapto-1,2,4-triazole, the ligand can exist in both thiol and thione forms, as shown in figure 1.

There are four medium bands around 3230, 3190, 3050, 2950 cm^{-1} in the spectrum of the ligands due to υ(N–H) and $\upsilon(NH_2)$. The broadness of the band suggests intramolecular hydrogen bonding. No bands in the vicinity of 2500 cm^{-1} were observed, so the free ligands adopt the thione form [22]. This is further supported by

Table 1. Elemental analysis results and yields of **a–e**, **(1a)–(3a)**, **(1b)–(3b)**, **(1c)–(3c)**, **(1d)–(3d)** and **(1e)–(3e)**.

Schiff bases[a] and complexes[b]		Yield (%)	m.p. (°C)	Found (Calcd.) (%) (%) C	Found (Calcd.) (%) (%) H	Found (Calcd.) (%) (%) N
a	($C_9H_{10}N_6OS$)	80	250–258	43.17(43.19)	4.07(4.03)	33.56(33.58)
1a	($CrC_{14}H_{10}N_6O_6S$)	79	250–258	38.38(38.01)	2.01(2.28)	18.77(19.00)
2a	($MoC_{14}H_{10}N_6O_6S$)	82	250–255	34.23(34.58)	1.94(2.07)	17.40(17.28)
3a	($WC_{14}H_{10}N_6O_6S$)	84	253–257	29.12(29.29)	1.54(1.75)	14.65(14.64)
b	($C_{13}H_{12}N_6OS$)	70	258–262	52.02(51.99)	4.00(4.03)	27.93(27.98)
1b	($CrC_{18}H_{12}N_6O_6S$)	78	258–262	43.61(43.91)	2.25(2.46)	17.49(17.07)
2b	($MoC_{18}H_{12}N_6O_6S$)	82	250–255	40.15(40.31)	2.10(2.26)	15.29(15.67)
3b	($WC_{18}H_{12}N_6O_6S$)	82	250–255	34.16(34.63)	1.76(1.94)	13.96(13.46)
c	($C_9H_{10}N_6OS$)	85	250–255	42.16(43.19)	4.09(4.03)	33.55(33.58)
1c	($CrC_{14}H_{10}N_6O_6S$)	80	250–258	38.69(38.01)	2.44(2.28)	18.89(19.00)
2c	($MoC_{14}H_{10}N_6O_6S$)	82	250–255	34.94(34.58)	1.96(2.07)	17.55(17.28)
3c	($WC_{14}H_{10}N_6O_6S$)	84	253–257	29.54(29.29)	1.39(1.76)	14.19(14.64)
d	($C_9H_{10}N_6OS$)	75	253–257	43.20(43.19)	4.05(4.03)	33.93(33.58)
1d	($CrC_{14}H_{10}N_6O_6S$)	80	250–258	38.50(38.01)	2.93(2.28)	19.16(19.00)
2d	($MoC_{14}H_{10}N_6O_6S$)	82	250–255	34.32(34.58)	2.64(2.07)	17.30(17.28)
3d	($WC_{14}H_{10}N_6O_6S$)	74	253–257	29.42(29.29)	1.91(1.76)	14.52(14.64)
e	($C_9H_9BrN_6OS$)	75	260–264	32.81(32.84)	2.75(2.76)	24.55(25.53)
1e	($CrC_{14}H_9BrN_6O_5S$)	80	260–264	33.89(33.28)	1.95(1.80)	16.37(16.63)
2e	($MoC_{14}H_9BrN_6O_5S$)	70	260–269	30.84(30.62)	1.76(1.65)	15.53(15.30)
3e	($WC_{14}H_9BrN_6O_5S$)	85	260–264	26.94(26.39)	1.182(1.42)	13.53(13.19)

[a,b] Light yellow.

the appearance of a band around 930 cm^{-1} assignable to υ(C=S) [23–25]. A very strong band around 1635 cm^{-1} in the spectra of the ligands is due to δ(NH) [26]. A broad band around 1600 cm^{-1} can be assigned to υ(C=N) of the exocyclic and endocyclic C=N moieties [26]. The ligands contain a thioamide moiety H–N–C=S and give rise to four characteristic bands in IR spectra. The thioamide band I has a major contribution from υ(N–H) and a minor contribution from υ(C=N), and is observed at 1500–1460 cm^{-1} in the spectra of the ligands. If charge delocalization occurs between C and N, a shift in band position towards higher wavenumber would be expected. If the contribution from υ(C=N) is minor, the shift would be small and the overall effect could be a shift towards lower wavenumber. The thioamide band II has a major contribution from υ(C=N) and is observed at 1346–1315 cm^{-1}. The thioamide band III has a major contribution from υ(C=N) and a minor contribution from υ(C=S) in the region 1105–1155 cm^{-1} in the spectra of the ligands. The thioamide band IV is almost solely from υ(C=S) around 730–784 cm^{-1} [27].

The bands due to NH_2 groups and NH–NH_2 remain unaffected but the S–H bands occur around 2220 cm^{-1}, while the ring N–H band disappears in the region of 3030 cm^{-1} due to complexation. This conclusion is further supported by the disappearance of υ(C=S) in the complexes and the appearance of a υ(C–S) band around 815 cm^{-1} [23]. Furthermore, the ligand also displays a band around 1607 (endocyclic) and 1590 (exocyclic) cm^{-1} due to υ(C=N) and this exocyclic υ(C=N) band shifts to 1560 cm^{-1} in the complexes indicating that the nitrogen is involved in coordination to the metal carbonyl [21, 22], whereas the endocyclic υ(C=N) band remains unperturbed. Coordination of metal carbonyl through nitrogen of the azomethine group (exocyclic υ(C=N)) of the thiol form of the ligands results in formation of a second endocyclic υ(C=N) band around 1615 cm^{-1}. Furthermore, the

Table 2. Important infrared spectral bands (cm^{-1}) of **a**–**e**, (**1a**)–(**3a**), (**1b**)–(**3b**), (**1c**)–(**3c**), (**1d**)–(**3d**) and (**1e**)–(**3e**).

Schiff bases and complexes	$\upsilon_{(NHNH2)}$	$\upsilon_{(NH)}$ (endo.)	$\upsilon_{(S\text{–}H)}$	υ(CO)	$\delta_{(NH)}$	$\upsilon_{(C=N)}$ (endo.)	$\upsilon_{(C=N)}$ (exo.)	T_1	T_2	T_3	T_4	$\upsilon_{(C=S)}$	$\upsilon_{(C\text{–}S)}$
a	3276(w), 3154(m), 2954(w)	3050(br)	–	–	1638(br)	1607(br)	1590(sh)	1476(br)	1330(br)	1130(m)	761(m)	962(m)	–
1a	3276(w), 3146(m), 2954(w)	–	2223(w)	2061(w), 1923(br), 1880(sh)	1638(br)	1615(br), 1607(sh)	1560(sh)	1476(br)	1369(w)	1192(m), 1038(m)	761(m)	–	815(w)
2a	3276(w), 3150(m), 2954(w)	–	2225(w)	2069(w), 1930(br), 1889(sh)	1638(br)	1616(br), 1607(sh)	1564(sh)	1474(br)	1366(w)	1190(m), 1040(m)	760(m)	–	818(w)
3a	3276(w), 3152(m), 2954(w)	–	2228(w)	2084(w), 1923(br), 1885(sh)	1638(br)	1612(br), 1607(sh)	1570(sh)	1478(br)	1365(w)	1186(m), 1036(m)	756(m)	–	815(w)
b	3300(w), 3192(m), 2953(w)	3023(br)	–	–	1646(br)	1607(br)	1590(sh)	1476(br)	1315(br)	1153(m)	769(m)	946(m)	–
1b	3300(w), 3199(br)–2953(w)	–	2284(w)	2061(w), 1930(br), 1885(sh)	1646(br)	1620(sh), 1607(m)	1561(m)	1446(w)	1376(w)	1184(m), 1038(m)	761(m)	–	823(w)
2b	3300(w), 3192(m), 2953(w)	–	2286(w)	2069(w), 1930(br), 1889(sh)	1646(br)	1622(sh), 1607(m)	1564(m)	1448(w)	1380(w)	1190(m), 1040(m)	766(m)	–	820(w)
3b	3300(w), 3192(m), 2953(w)		2280(w)	2084(w), 1923(br), 1885(sh)	1646(br)	1618(sh), 1607(m)	1560(m)	1445(w)	1370(w)	1182(m), 1036(m)	764(m)	–	820(w)
c	3230(w), 3192(br), 2953(w)	3023(w)	–	–	1638(sh)	1607(sh)	1592(br)	1500(br) 1461(w)	1330(br)	1107(m)	784(m)	923(m)	–
1c	3230(w), 3192(br), 2961(w)	–	2207(w)	2061(w), 1976(br), 1910(sh)	1638(sh)	1623(br), 1607(sh)	1565(sh)	1446(w)	1370(w)	1169(m), 1107(m)	792(m)	–	861(w)
2c	3230(w), 3192(br), 2952(w)	–	2210(w)	2069(w), 1980(br), 1890(sh)	1638(sh)	1625(br), 1607(sh)	1561sh)	1448(w)	1376(w)	1172(m), 1106(m)	788(m)	–	860(w)
3c	3230(w), 3192(b), 2960(w)	–	2215(w)	2084(w), 1976(br), 1910(sh)	1638(sh)	1621(br), 1607(sh)	1560(sh)	1446(w)	1380(w)	1180(m), 1100(m)	790(m)	–	860(w)
d	3238(w), 3184(br), 2953(w)	3023(w)	–	–	1638(sh)	1607(br)	1592(br)	1500(br)	1330(br)	1115(br)	784(m)	923(m)	–
1d	3238(w), 3192(br), 2923(w)	–	2215(m)	2069(w), 1923(br), 1890(sh)	1638(sh)	1623(br), 1607(sh)	1565(sh)	1507(m)	1369(w)	1184(m), 1053(w)	753(w)	–	823(w)
2d	3238(w), 3184(br), 2945(w)	–	2210(m)	2084(w), 1930(br), 1880(sh)	1638(sh)	1624(br), 1607(sh)	1570(sh)	1460(w)	1372(w)	1190(m), 1060(m)	760(w)	–	823(w)
3d	3238(w), 3190(br), 2940(w)	–	2207(m)	2090(w), 1936(br), 1880(sh)	1638(sh)	1620(br), 1607(sh)	1564(sh)	1446(w)	1376(w)	1192(m), 1052(m)	755(w)	–	823(w)
e	3307(w), 3192(br), 2946(w)	3030(w)	–	–	1650(sh)	1600(br)	1590(sh)	1484br)	1315(br)	1123(br)	730(m)	938(m)	–
1e	3307(w), 3192(br), 2955(w)	–	2200(w)	2061(w), 1923(br), 1890(sh)	1650(sh)	1615(sh), 1600(br)	1561(br)	1469(m) 1453(w)	1369(sh)	1184(m), 1038(br)	723(w)	–	815(m)
2e	3307(w), 3192(br), 2950(w)	–	2210(w)	2069(w), 1930(br), 1880(sh)	1650(sh)	1618(sh), 1600(br)	1565(br)	1470(m) 1450(w)	1370(sh)	1190(m), 1040(br)	734(w)	–	815(m)
3e	3307(w), 3192(br), 2955(w)	–	2207(w)	2084(w), 1940(br), 1910(sh)	1650(sh)	1612(sh), 1600(br)	1560(br)	1466(m) 1448(w)	1362(sh)	1182(m), 1036(br)	721(w)	–	815(m)

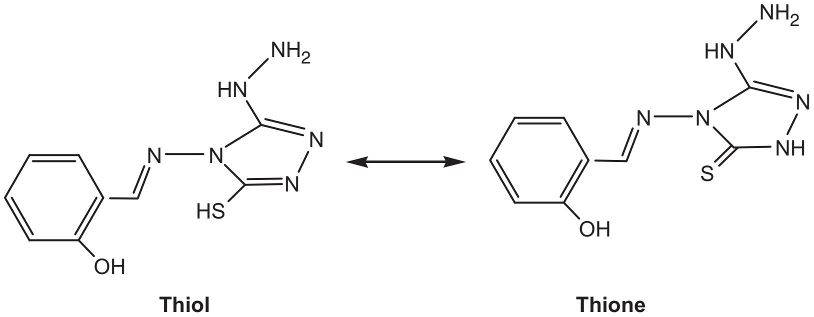


Figure 1. Thione and thiol form of a Schiff base.

four characteristic thioamide bands in the spectra of the ligand molecules change upon complexation. Because of the tautomerism of the thioamide moiety and the redistribution of the electron cloud, as a result of complex formation, there is a systematic shift in these bands in the IR spectra of the complexes as compared to those of the ligand, consistent with the coordinating ability of the exo-imine atom to the metal [21, 27].

As expected, three bands arising from ν(CO) vibrations are seen for the complexes which have local C_{4v} $(2A_1+E)$ symmetry of the $M(CO)_5$ unit (M = Cr, Mo, W). The ν(CO) modes move to lower wavenumbers compared with the starting $M(CO)_6$ (M = Cr, Mo, W) molecules [28–32].

^{1}H and ^{13}C NMR spectral data in DMSO-d_6 solutions of the compounds are collected in tables 3 and 4. The ^{1}H NMR spectra for the ligands show five signals around 13.00, 11.00, 10.00, 8.50 and 5.50 ppm relative to TMS, assigned to the NH endocyclic, OH and NH exocyclic and NH_2 protons, respectively [33, 34]. The signal due to SH of the coordinated ligands appears around 4.50 ppm and the signal due to NH endocyclic disappears, indicating that the coordinated ligand is in the thiol form. The signal around 8.50 ppm due to azomethine proton [(H–C=N) exocyclic] is shifted downfield in the spectra of the **(1a)**–**(3a)**, **(1b)**–**(3b)**, **(1c)**–**(3c)**, **(1d)**–**(3d)** and **(1e)**–**(3e)** complexes. The small shift for [(H–C=N) exocyclic] proton may be related to decreasing π-electron density in the C=N bond with complex formation [30], also indicating coordination of the ligands through azomethine nitrogen. ^{13}C NMR spectra show four signals at 165.00, 159.00, 150.00 and 145.00 ppm, which are assigned to the (C–OH), (C=S) and (C=N) endocyclic, (H–C=N) exocyclic carbons, respectively. The signal due to the second (C=N) endocyclic of the coordinated ligands appears around 160 ppm, whereas the signal due to (C=S) disappears in the complexes, also indicating the coordinated ligand is in the thiol form. The signal around 145.00 ppm due to azomethine carbon [(H–C=N) exocyclic] shifts upfield in the spectra of **(1a)**–**(3a)**, **(1b)**–**(3b)**, **(1c)**–**(3c)**, **(1d)**–**(3d)** and **(1e)**–**(3e)**. The small shift for [(H–C=N) exocyclic] may be related to decreasing π-electron density in the C=N bond with complex formation [29]. According to these data, the ligands coordinate monodentate through azomethine nitrogen [(H–C=N) exocyclic] to the metal carbonyls.

The mass spectral data of **(1a)**–**(3a)**, **(1b)**–**(3b)**, **(1c)**–**(3c)**, **(1d)**–**(3d)** and **(1e)**–**(3e)** given in table 5 show fragmentation via successive loss of CO groups and organic ligands.

Table 3. ^{1}H NMR spectroscopic data for **a**–**e**, (**1a**)–(**3a**), (**1b**)–(**3b**), (**1c**)–(**3c**), (**1d**)–(**3d**) and (**1e**)–(**3e**) in DMSO-d$_6$ (ppm).

Schiff bases and complexes	δ (NH)$_{endocyclic}$	δ(OH)$_{ring}$	δ (NH)$_{exocyclic}$	δ (H–C=N)$_{exocyclic}$	δ (C–H)$_{ring}$	δ (–NH$_2$)$_{hydrazine}$	δ (SH)$_{endocyclic}$
a	12.95, s, 1H	10.93, s, 1H	10.84, s, 1H	8.47, s, 1H	7.39; 7.24; 6.88; 6.84, (4H)	5.48, s, 2H	–
1a	–	11.00, s, 1H	10.92, s, 1H	8.55, s, 1H	7.47; 7.30; 6.95; 6.91, (4H)	5.56, s, 2H	4.31, s, 1H
2a	–	11.08, s, 1H	10.71, s, 1H	8.62, s, 1H	7.32; 7.12; 6.93; 6.90, (4H)	5.62, s, 2H	4.30, s, 1H
3a	–	11.09, s, 1H	10.99, s, 1H	8.48, s, 1H	7.45; 7.33; 6.99; 6.91, (4H)	5.60, s, 2H	4.25, s, 1H
b	13.00, s, 1H	12.13, s, 1H	10.96, s, 1H	9.39, s, 1H	8.14; 7.86; 7.58; 7.54; 7.37; 7.15, (6H)	5.50, br, 2H	–
1b	–	12.14, s, 1H	10.97, s, 1H	9.43, s, 1H	8.20; 8.12; 7.90; 7.58; 7.40; 7.17, (6H)	5.55, s, 2H	4.15, s, 1H
2b	–	12.16, s, 1H	10.94, s, 1H	9.40, s, 1H	8.31; 8.10; 7.75; 7.48; 7.40; 7.10, (6H)	5.50, s, 2H	4.29, s, 1H
3b	–	12.13, s, 1H	10.97, s, 1H	9.35, s, 1H	8.27; 8.16; 7.92; 7.32; 7.30; 7.11, (6H)	5.42, s, 2H	4.32, s, 1H
c	13.00, s, 1H	10.52, s, 1H	9.48, s, 1H	8.20, s, 1H	7.20; 7.16; 6.97; 6.75, (4H)	5.45, s, 2H	–
1c	–	9.55, br, 1H	9.18, s, 1H	8.22, s, 1H	7.23; 7.21; 6.98; 6.61, (4H)	5.48, s, 2H	4.26, s, 1H
2c	–	9.62, br, 1H	9.24, s, 1H	8.20, s, 1H	7.26; 7.20; 6.90; 6.54, (4H)	5.47, s, 2H	4.34, s, 1H
3c	–	9.59, br, 1H	9.20, s, 1H	8.18, s, 1H	7.34; 7.18; 6.96; 6.50, (4H)	5.45, s, 2H	4.28, s, 1H
d	12.83, s, 1H	10.29, s, 1H	9.73, s, 1H	8.18, s, 1H	7.40; 6.77, (4H)	5.43, s, 2H	–
1d	–	11.03, s, 1H	9.73, s, 1H	8.26, s, 1H	7.68; 6.85, (4H)	5.55, s, 2H	4.32, s, 1H
2d	–	11.00, s, 1H	9.81, s, 1H	8.32, s, 1H	7.66; 6.82, (4H)	5.45, s, 2H	4.35, s, 1H
3d	–	11.09, s, 1H	9.76, s, 1H	8.24, s, 1H	7.64; 6.80, (4H)	5.58, s, 2H	4.30, s, 1H
e	12.97, s, 1H	11. 03, s, 1H	10. 83, s, 1H	8.44, s, 1H	7.64; 7.35; 7.33; 6.84, (4H)	5.48, s, 2H	–
1e	–	10.96, s, 1H	10.88, s, 1H	9.39, s, 1H	7.70; 7.46; 7.30; 7.20, (4H)	5.50, s, 2H	4.24, s, 1H
2e	–	11.06, s, 1H	10.85, s, 1H	9.42, s, 1H	7.62; 7.38; 7.28; 7.20, (4H)	5.46, s, 2H	4.21, s, 1H
3e		10.98, s, 1H	10.78, s, 1H	9.36, s, 1H	7.69; 7.41; 7.37; 7.24, (4H)	5.51, s, 2H	4.24, s, 1H

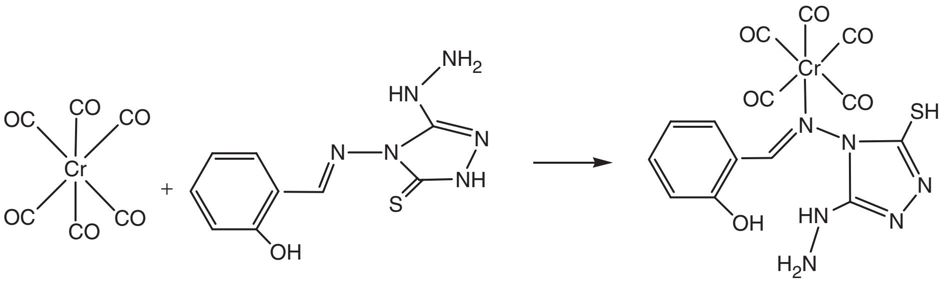
Table 4. ^{13}C -{^1H} NMR spectroscopic data for **a**–**e**, (**1a**)–(**3a**), (**1b**)–(**3b**), (**1c**)–(**3c**), (**1d**)–(**3d**) and (**1e**)–(**3e**) in DMSO-d_6 (ppm).

Schiff bases and complexes	δ(CO)	δ (C–OH) $_{benz}$	δ(S–C=N)$_{endo}$	δ(C=S)	δ(C=N)$_{endo}$	δ(C=N)$_{exo}$	δ(C–H)$_{ring}$
a	–	165.55	–	157.48	150.21	145.99	131.18; 129.69 119.99; 119.66; 116.97
1a	205.17; 201.93; 192.73; 191.71; 187.26	165.54	164.73	–	150.21	142.31	130.94; 128.40 120.87; 119.89; 116.71
2a	207.67; 202.56 190.88; 189.55; 186.12	165.66	164.13	–	150.76	142.54	131.12; 128.34 121.31; 119.78; 116.61
3a	206.54; 200.62 191.78; 190.34; 188.12	165.23	164.46	–	150.56	142.67	130.78; 128.34 120.74; 119.13; 116.55
b	–	165.76	–	157.60	150.14	144.70	132.48, 132.09; 129.58; 128.24 123.13; 121.31; 119.48; 109.53
1b	210.8; 205.17 196.60; 192.73; 186.20	165.53	162.54	–	150.12	141.94	133.31; 130.55; 122.48; 119.20 113.56; 111.11; 110.20; 106.99
2b	209.12; 206.87 194.45; 192.67; 188.56	165.23	161.92	–	150.29	142.04	134.56; 131.12; 121.91; 120.89 114.56; 112.45; 110.23; 105.89
3b	208.98; 204.45 197.29; 193.78; 185.49	165.71	162.46	–	150.52	141.15	133.56; 131.92; 129.01; 110.17 115.04; 110.97; 109.92; 105.34
c	–	164.13	–	159.45	150.20	145.73	132.70; 128.56 124.61; 116.98; 112.34
1c	204.37; 201.62 194.88; 192.88; 184.13	164.30	166.39	–	152.15	136.16	133.91; 129.67 123.92; 118.42; 113.68
2c	206.71; 200.39 195.45; 191.32; 182.56	164.02	166.51	–	152.39	135.96	132.84; 130.31 124.48; 120.50; 114.15
3c	203.32; 202.04 196.31; 192.45; 184.45	164.61	166.09	–	152.41	136.34	134.12; 131.17 124.56; 118.91; 112.98
d	–	164.94	–	159.36	150.46	145.24	128.73 126.44; 116.27
1d	228.19; 209.90 192.99; 189.91; 182.20	164.50	162.55	–	150.43	142.31	129.05 126.60; 115.99
2d	227.43; 208.12 193.24; 190.71; 184.19	164.19	162.71	–	150.13	142.61	130.18 126.91; 114.89
3d	226.48 194.18; 186.35; 183.01	164.28	162.89	–	150.72	142.55	129.91 125.66; 114.31
e	–	165.54	–	156.37	150.11	143.01	133.30; 130.55 122.45; 119.20; 111.12
1e	209.91; 201.12 195.29; 187.02; 182.20	166.51	159.15	–	150.43	137.47	133.01; 131.19 125.58; 119.72; 111.71
2e	210.21; 201.13 194.56; 188.10; 181.81	165.92	159.42	–	150.15	137.82	134.12; 132.41 124.52; 120.04; 110.96
3e	209.51; 200.92 196.14; 189.45; 180.39	165.27	159.33	–	150.20	138.03	133.45; 131.16 126.71; 119.92; 109.86

Table 5. The mass spectral data of (**1a**)–(**3a**), (**1b**)–(**3b**), (**1c**)–(**3c**), (**1d**)–(**3d**) and (**1e**)–(**3e**).

Schiff bases and complexes	M.W.	Relative intensities of the ions m/e and assignment[a]
a	251	251 (80), $[M^+]$
1a	442	442 (5), $[M^+]$; 424 (5), $[M^+-(OH)]$; 371 (10) $[M^+-(OH+2CO)]$
2a	486	486 (4), $[M^+]$; 458 (5), $[M^+-(CO)]$; 402 (5), $[M^+-(3CO)]$
3a	574	574 (10), $[M^+]$; 558 (10), $[M^+-(NH_2)]$; 503 (20), $[M^+-(NH_2+2CO)]$
b	300	300 (80), $[M^+]$
1b	492	492 (10), $[M^+]$; 460(20), $[M^+-SH]$; 404 (10), $[M^+-(SH+2CO)]$
2b	536	536 (5), $[M^+]$; 508 (5), $[M^+-(CO)]$; 480 (5), $[M^+-(2CO)]$
3b	624	624 (5), $[M^+]$; 596 (7), $[M^+-(CO)]$; 568 (5), $[M^+-(2CO)]$
c	251	251 (85), $[M^+]$
1c	442	442 (5), $[M^+]$; 424 (5), $[M^+-(OH)]$; 371 (10), $[M^+-(OH+2CO)]$
2c	486	486 (4), $[M^+]$; 458 (5), $[M^+-(CO)]$; 402 (5), $[M+-(3CO)]$
3c	574	574 (10), $[M^+]$; 558 (10), $[M^+-(NH_2)]$; 503 (20), $[M^+-(NH_2+2CO)]$
d	251	251 (90), $[M^+]$
1d	442	442 (5), $[M^+]$; 424 (5), $[M^+-(OH)]$; 371 (10), $[M^+-(OH+2CO)]$
2d	486	486 (4), $[M^+]$; 458 (5), $[M^+-(CO)]$; 402 (5), $[M^+-(3CO)]$
3d	574	574 (10), $[M^+]$; 558 (10), $[M^+-(NH_2)]$; 503 (20), $[M^+-(NH_2+2CO)]$
e	329	329 (80), $[M^+]$
1e	505	505 (5), $[M^+]$; 489 (15), $[M^+-NH_2]$; 461 (15), $[M^+-(NH_2+CO]$; 434 (10), $[M^+-(NH_2+2CO]$
2e	549	549 (4), $[M^+]$; 455 (15), $[M^+-(NHNH_2+SH+CO)]$
3e	637	637 (4), $[M^+]$; 511 (20), $[M^+-(NHNH_2+SH+2CO)]$

[a] For the mass spectral data relative intensities are given in parenthesis; probable assignments in square brackets. For all assignments the most abundant isotopes of Cr, Mo, W have been selected (^{52}Cr, 83.76%, ^{98}Mo, 24%, ^{184}W, 30.7%, abundant).



Scheme 1. The photochemical reactions of VIB $Cr(CO)_6$ with SAHMT.

4. Conclusions

We prepared heterocyclic Schiff bases, **a**–**e**, and their VIB metal carbonyl $[M(CO)_6]$ (M = Cr, Mo, W) complexes by photochemical reactions. The ligand molecule exists in both thione and thiol forms due to tautomerism with the most effective (+M) mesomeric effect for the thiol form. Thus, extended delocalization of the triazole ring could reach the azomethine group to compensate electron deficiency due to coordination of azomethine nitrogen to metal carbonyl. The spectral data indicate the Schiff bases derived from 1,2,4-triazole, **a**–**e**, are monodentate, coordinating to the metal via azomethine nitrogen [(H–C=N) exocyclic] as shown in scheme 1. Schiff bases **a**–**e** are 2-electron donors to satisfy the 18–electron rule.

Acknowledgements

This research was supported by Ege University Research Funds, Project No: 019/Fen/2003, Istanbul University Research Funds, Project No: T-977/19022001 and TUBITAK, Project No: 104T206.

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