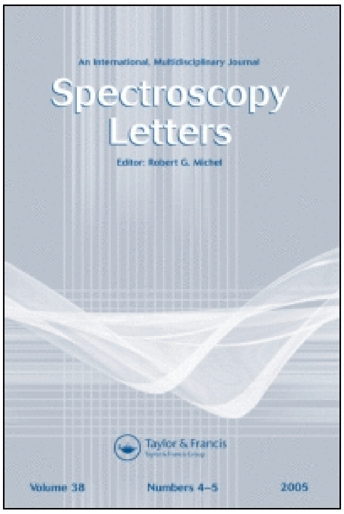

Spectroscopy Letters
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713597299

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To cite this Article El-Medani, S. M. , Aboaly, M. M. , Abdalla, H. H. and Ramadan, R. M.(2004) 'Reactions of Group 6 Metal Carbonyls with Salicylaldehyde Hydrazone', Spectroscopy Letters, 37: 6, 619 — 632
To link to this Article: DOI: 10.1081/SL-200037610
URL: http://dx.doi.org/10.1081/SL-200037610

SPECTROSCOPY LETTERS
Vol. 37, No. 6, pp. 619–632, 2004

Reactions of Group 6 Metal Carbonyls with Salicylaldehyde Hydrazone

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ABSTRACT

The interaction of salicylaldehyde hydrazone (shH) with $Cr(CO)_6$ in the absence of oxygen resulted in the formation of the tris derivative $Cr(sh)_3$, **1**. Reactions of $M(CO)_6$, M = Cr, Mo in air gave the oxo derivatives $M(O)(sh)_2$, **2** and **3**, with the metal atom in +4 formal oxidation state. Prolonged heating of a mixture of $Mo(CO)_6$ and shH in air resulted in the formation of the dinuclear complex $Mo_2(O)_6(shH)$, **4**. Structures for the complexes were proposed based on the spectroscopic studies. Reactions of $W(CO)_6$ with shH in air or under reduced pressure lead to the formation of the salicylaldehyde azine dimer via elimination of a

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DOI: 10.1081/SL-200037610 0038-7010 (Print); 1532-2289 (Online)

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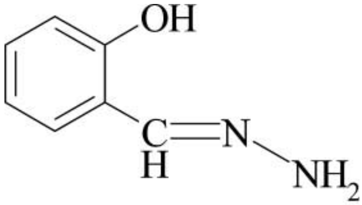
hydrazine molecule. The structure of the dimer was confirmed by crystal structure determination and by FTIR and FT-Raman spectroscopy.

Key Words: Chromium; Molybdenum; Tungsten; Hydrazones; Crystal structure; Spectra.

INTRODUCTION

Transition metal carbonyl derivatives are used as catalysts in many catalytic reactions such as carbonylation, hydrogenation, and hydroformylation reactions.[1–3] On the other hand, molybdenum is also involved in complexes, that catalyze nitrogen fixation in plants by some microorganism.[4] Hydrazones have been extensively investigated due to their potential applications as antiviral or anti-inflammatory agents either in the free or in the metal complexed states.[5–7] Reactions of transition metal ions with hydrazones such as salicylaldehyde hydrazone (shH) and its derivatives have been thoroughly investigated.[8–16] The importance of hydrazones as complexing agents, and the catalytic role of metal carbonyls in organic and organometallic synthesis[17–21] have prompted us to investigate the reactions of (shH) with group 6 metal carbonyls. In this paper, we report the synthesis and structural studies of the complexes isolated from the reactions of $M(CO)_6$, M = Cr and Mo, with the shH ligand. The catalytic effect of $W(CO)_6$ on shH, which led to the formation of salicylaldehyde azine via dimerization, is also discussed.



Salicylaldehyde hydrazone (shH)

EXPERIMENTAL

Reagents

$M(CO)_6$, M = Cr, Mo, and W, were supplied from Aldrich. The ligand shH was prepared as described in the literature.[22] All solvents were of analytical grade and purified by distillation before use.

Physical Measurements

IR measurements (KBr pellets) were carried out on a Unicam-Mattson 1000 FT-IR spectrometer. Raman measurements for the solid samples were performed on a Nicolet FT-Raman spectrometer equipped with a YAG laser of wavelength 1064 nm using a laser power of ca. 200 mW. ^{1}H NMR measurements were carried out on a Spectrospin-Bruker AC 200 MHz NMR spectrometer. The samples were dissolved in deuterated DMSO using TMS as an internal reference. Magnetic susceptibilities of the paramagnetic complexes in the solid state (Gouy method) were recorded on a Sherwood magnetic susceptibility balance. Diamagnetic corrections were made by Pascal's constant and $Hg[Co(SCN)_4]$ was used as a calibrant. Elemental analyses were carried out on a Perkin–Elmer 2400 CHN elemental analyzer. mass spectra of the complexes (70 eV, EI) were performed on a Finnigan MAT SSQ 7000 spectrometer.

Preparation of the Ligand and the Complexes

The ligand shH was prepared by slowly adding 0.1 mol of salicylaldehyde dissolved in ethanol to 0.1 mol of hydrazine hydrate in 50 cm^3 ethanol. The mixture was shaken thoroughly after each addition, refluxed for an hour on a water-bath and cooled, the hydrazone was then separated. The product was recrystallized from methanol giving creamy white crystalline needles (m.p. 94–95°C, yield 82%). The characteristic IR and Raman data of shH are given in Table 1.

Synthesis of $Cr(sh)_3$ Complex

$Cr(CO)_6$ (0.10 g, 0.45 mmol), shH (0.18 g, 1.32 mmol), and ca. 30 cm^3 THF were introduced in a sealed tube, degassed, and then heated for 12 hr. The reaction mixture was cooled and the solvent was then removed on a vacuum line. The residue was washed several times with boiling petroleum ether and then crystallized from hot ethanol to give brown crystals. The complex was left to dry under vacuum for several hours (yield 74%). The identical product was obtained when the reaction was carried out in absolute EtOH. Anal. Calc. (found) for $C_{21}H_{21}O_3N_6Cr$ (%): C, 55.1 (55.3); H, 4.6 (4.5); N, 18.4 (18.7). The mass spectrum of the complex showed a molecular ion peak at m/z 458 (P^+).

Table 1. Important IR and Raman data for shH and important IR data for the complexes.

	IR data (cm^{-1})						
Compound	ν(OH)	$\nu(NH_2)$	$\delta(NH_2)$	$\gamma(NH_2)$	ν(C=N)	δ(OH)	ν(C–O)
ShH	3250w	3384s (3289m)	1574s (1575m)	707s (709sh)	1608m (1607s)	1406s (1408w,b)	1275s (1276w)
$Cr(sh)_3$	—	3337m	1544m	644m	1618s	—	1298s
$CrO(sh)_2$[a]	—	3299m	1538m	667w	1619s	—	1273w, 1317m
$MoO(sh)_2$[b]	—	3446m,b	1545w	682w	1621s	—	1274m
$Mo_2O_6(shH)$[c]	3174(b)	3424m,b	1545w	714m	1614s	1404m	1275m

Note: Raman frequencies are given between parenthesis. s, strong; m, medium; w, weak; b, broad.

[a] $\nu(Cr{=}O) = 894\,cm^{-1}$.

[b] $\nu(Mo{=}O) = 897\,cm^{-1}$.

[c] $\nu_s(MoO_2) = 938\,cm^{-1}$(cis); $\nu_{as}(MoO_2) = 898\,cm^{-1}$ (cis), $\nu_s(Mo{-}O{-}Mo) = 472\,cm^{-1}$, $\nu_{as}(Mo{-}O{-}Mo) = 822\,cm^{-1}$.

Synthesis of $Cr(O)(sh)_2$ Complex

A mixture of $Cr(CO)_6$ (0.10 g, 0.45 mmol) and shH (0.12 g, 0.88 mmol) in ca. 25 cm^3 absolute EtOH was heated to reflux under atmospheric pressure in air for 8 hr. The color of the reaction mixture changed from yellow to orange and finally to brown. The reaction mixture was cooled and the solvent was removed on a vacuum line. The residue was washed several times with boiling petroleum ether and then crystallized from hot ethanol to give a brown solid. The complex was left to dry in vacuo for few hours (yield 65%). Anal. Calc. (found) for $C_{14}H_{14}O_3N_4Cr$ (%): C, 49.7 (49.5); H, 4.2 (4.3); N, 16.6 (16.8). A molecular ion peak was observed for the complex in its mass spectrum at m/z 339 (P^+).

Synthesis of $Mo(O)(sh)_2$ Complex

A similar procedure was employed as for $Cr(O)(sh)_2$ but the reaction period was 1 hr. A brown solid was obtained (yield 62%). Anal. Calc. (found) for $C_{14}H_{14}O_3N_4Mo$ (%): C, 44.0 (43.8); H, 3.7 (3.8); N, 14.7 (14.5). A molecular ion peak was observed for the complex at m/z 383 (P^+) in the mass spectrum.

Synthesis of $Mo_2O_6(shH)$ Complex

A similar procedure was employed as for $Cr(O)(sh)_2$ but the reaction period was 5 hr. A dark brown solid was obtained (yield 83%). Anal. Calc. (found) for $Mo_2O_7N_2C_7H_8$ (%): C, 19.8 (19.5); H, 1.9 (2.0); N, 6.6 (6.8). A molecular ion peak was observed for the complex at m/z 425 (P^+) in the mass spectrum.

X-ray Structure Determination

The crystallographic data for x-ray analysis of salicylaldehyde azine are presented in Table 2. Atomic positional parameters, bond lengths, and angles, anisotropic temperature factors and the calculated and observed structure factors are given in Supplementary Tables (CCDC No: 227334). All diagrams and calculations were performed using maXus crystallographic software package (Nonius, Delft & MacScience, Japan). The displacement factors of non-hydrogen atoms of the complex were refined anisotropically, whereas the hydrogen atoms were refined isotropically.

Table 2. Crystal parameters and x-ray diffraction data of salicylaldehyde azine.

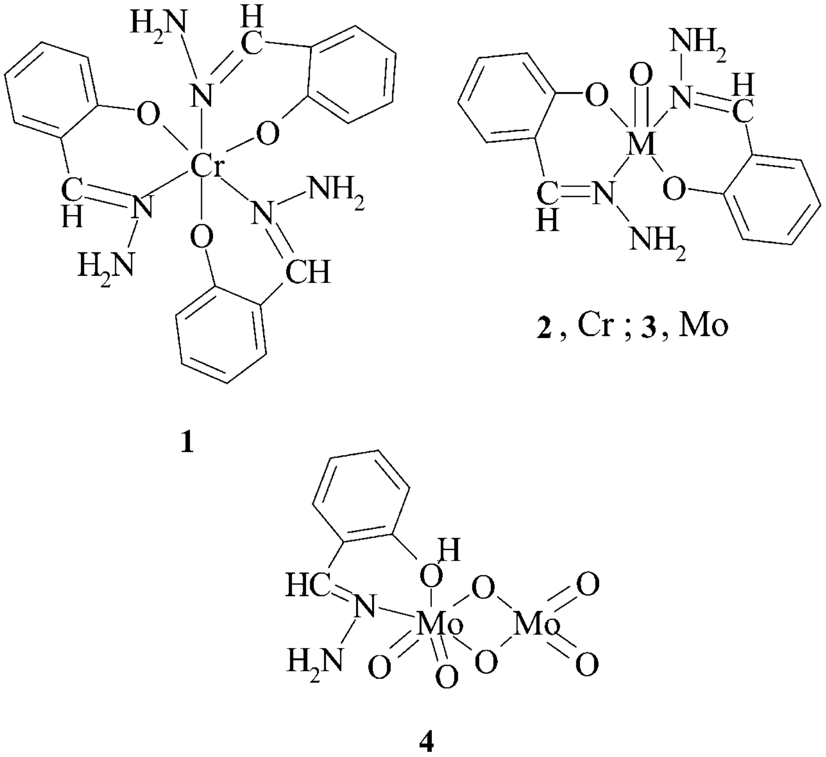
Empirical formula	$C_{14}H_{12}N_2O_2$
Fw	240.28
Crystal system	Monoclinic
Space group	$P2_1/c$
a (Å)	16.5351 (10)
b (Å)	5.9574 (3)
c (Å)	13.2616 (6)
α (°)	90.00
β (°)	113.462 (2)
γ (°)	90.00
V (Å^3)	1198.34 (11)
Z	4
T (K)	298
ρ_{calc} (g cm^{-3})	1.33
μ (cm^{-1})	0.09
R[a]	0.075
R_w[b]	0.090
(MoKα) (Å)	0.71073

[a] $R = \Sigma[|F_o| - |F_o| \, \Sigma \, |F_o|]$
[b] $R_w = [\Sigma_w(|F_o| - |F_c|)^2/\Sigma w \quad |F_o|^2]^{1/2}; \quad w = 1/\delta^2 \, (F_o)^2 + 0.10000 * (F_o)$.

RESULTS AND DISCUSSION

The interaction of shH with $M(CO)_6$, M = Cr and Mo, was found to be dependent on the reaction conditions. When the reaction of $Cr(CO)_6$ with shH was carried out in either absolute EtOH or THF in the absence of oxygen under reduced pressure, the tris derivative $Cr(sh)_3$ (**1**) was separated. On the other hand, an oxochromium complex, $Cr(O)(sh)_2$ (**2**) was isolated from reactions in absolute ethanol in air. The corresponding reaction of $Mo(CO)_6$ with shH in air (reaction time period 1 hr) resulted in the formation of the oxomolybdenum derivative $Mo(O)(sh)_2$ (**3**), while prolonged heating (5 hr) of the reaction in air gave a dinuclear complex with the molecular formula $Mo_2O_6(shH)$ (**4**). The IR and Raman spectra of shH ligand showed bands due to the OH, C=N, C–O, and NH_2 functional groups, Table 1. The IR spectra of the complexes exhibited the bands of the ligand with appropriate shifts due to complex formation (Table 1). However, the IR spectra of complexes **1**, **2**, and **3** did not show any bands due to the OH group, which indicated that the ligand was added to the metal oxidatively with proton displacement. The loss of the OH protons was also confirmed by ^{1}H NMR. In addition, the IR spectra of Cr(O)(sh)$_2$ and Mo(O)(sh)$_2$ displayed strong bands due to M=O stretching frequencies, Table 1. On the other hand, the two modes ν(OH) and δ(OH) of the ligand were observed in the IR spectrum of the oxo complex Mo_2O_6(shH), Table 1.[12,23,24] The IR spectrum of the complex also displayed two strong bands at 938 and 898 cm^{-1}, which are assigned owing to symmetric and asymmetric stretching frequencies of Mo=O bonds, respectively, for a cis MO_2 fragment of a dimeric structure having the core Mo_2O_6.[25,26]. In addition, the two stretches $\nu_{as}(Mo_2O)$ and $\nu_{s}(Mo_2O)$ of the oxo-bridging groups were observed at 822 and 472 cm^{-1}, respectively.[25] The ν(Mo–O) stretch (metal to ligand) was localized at 618 cm^{-1}. Several complexes having the Mo_2O_6 or Mo_2O_5 cores have been recently prepared, where molybdenum atom bonded to a cis dioxo group and the two Mo atoms were bridged by one or two oxygen atoms.[25,26]

The magnetic susceptibilities of the two chromium paramagnetic complexes in the solid state (**1** and **2**) were investigated using the Gouy method. The effective magnetic moment (μ_{eff}) of the tris complex Cr(sh)$_3$ gave a value of 4.53 BM as expected for Cr(III) species. On the other hand, the μ_{eff} value of the oxochromium complex **2** was found to be 1.82 BM. The latter value is lesser than the spin-only value for two unpaired electrons, which is expected for a d^{2} high-spin Cr(IV) species. However, many previously reported chromium(III) and chromium(IV) complexes showed smaller effective magnetic moments than the spin-only moments.[27,28] Investigation of the magnetic properties of the oxomolybdenum complex **3** showed that it was a diamagnetic. Such diamagnetism might arise from further splitting of the t_{2g} orbitals in the low symmetry complex with a low-spin d^{2} configuration.[24] Investigation of the dinuclear molybdenum complex **4** by ^{1}H NMR showed that the two singlets of the shH ligand at 11.34 and 7.94 ppm corresponding to the OH and CH=N protons were shifted to 10.25 and 8.99 ppm. This shift indicated that the shH ligand coordinates via its protonated OH group and the N atom of the CH = N moiety. From elemental analysis and the spectroscopic studies of complex **4**, it can be concluded that the shH ligand binds to only one Mo atom in a bidentate manner. Such structural arrangement was observed before with the molybdenum complex of the ligand 3-hydroxypicolinic acid.[26] The second Mo atom in **4** has two Mo=O in a cis form (Table 1), since the trans MO_2 moiety would exhibit only a single band in the IR spectrum at lower wavenumber, at ca. 850 cm^{-1}.[29] Apparently, the complex was stabilized by H-bonding between the OH of shH and the oxygen atom of the Mo=O group. Scheme 1 gives the proposed structures of the chromium and molybdenum complexes.



1

2, Cr ; **3**, Mo

4

Scheme 1.

The reaction between the W(CO)$_6$ and the ligand shH in air or under reduced pressure in ethanol or in THF led to the formation of a yellow crystalline product. Figure 1 shows the Raman spectrum of the obtained crystals. The IR and Raman spectra of the crystals are identical to those of salicylaldehyde azine.[23] Single crystal x-ray analysis of the compound was performed to confirm its structure. The ORTEP representation of the compound is illustrated in Fig. 2. The selected bond lengths and bond angles are given in Table 3. The data showed that salicylaldehyde azine crystallizes in the monoclinic system with a space group $P2_1/c$ and $Z = 4$. The bond lengths and bond angles are comparable to similar compounds.[13] The dihedral (torsional) angle of the skeleton (N–N–C=C) equals to 179.9° indicating an S-trans planar configuration for the central part.[22] However, the torsion angle N(27)–C(28)–C(13)–C(18) equals to 176.3° indicating that the phenyl ring is slightly tilted by about 3.6° (Table 3). The formation of

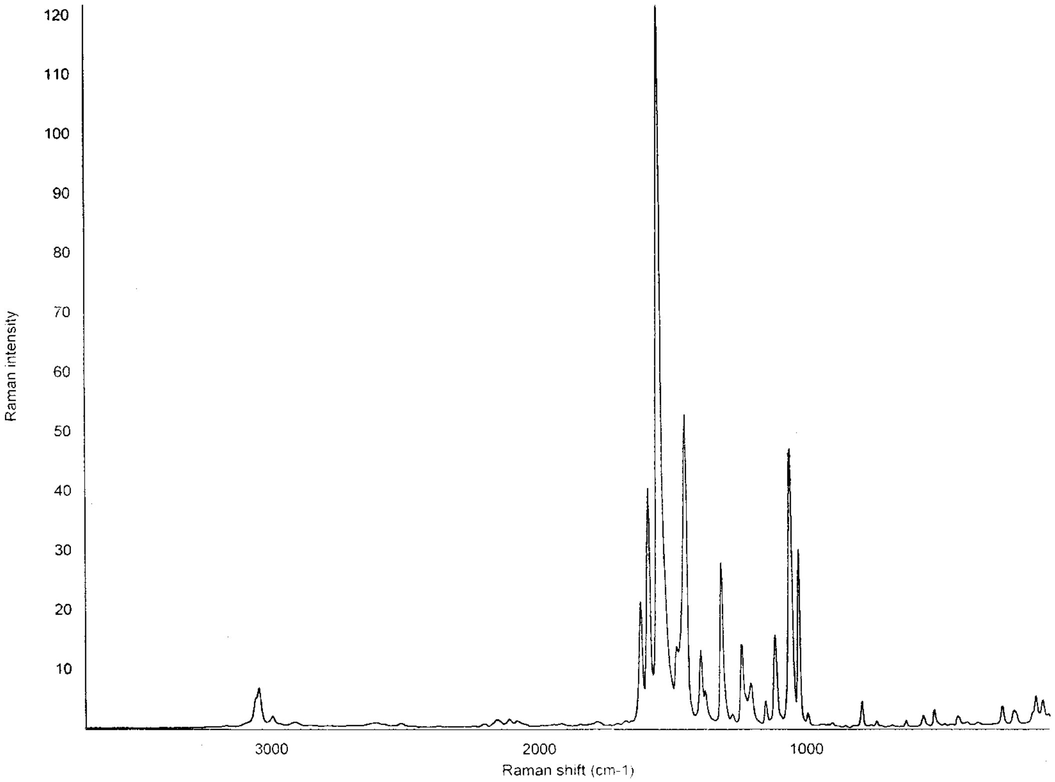


Figure 1. The Raman spectra of salicylaldehyde azine.

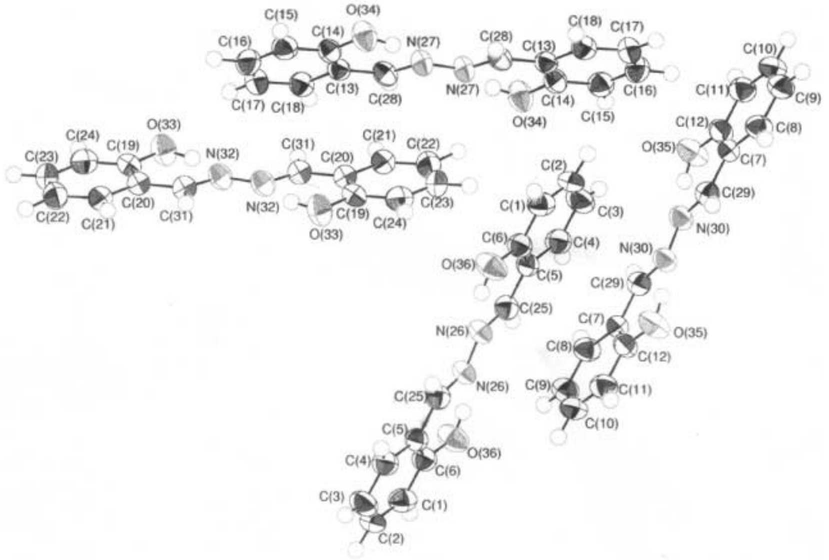
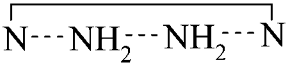


Figure 2. The ORTEP plot of salicylaldehyde azine (same number is given for equivalent atoms in each molecule).

salicylaldehyde azine from the shH ligand can be explained by dimer formation via the elimination of a hydrazine molecule ($NH_2{-}NH_2$); the reaction was catalyzed by $W(CO)_6$, Sch. 2. This dimer was presumably formed through the attack of an shH molecule on the tungsten complex with the formation of a tetracyclic intermediate:

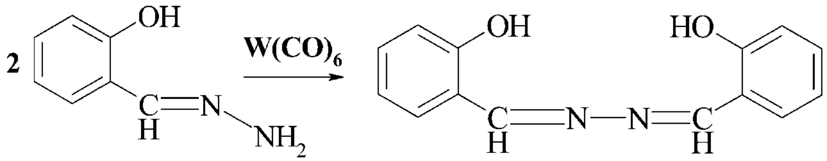


$$N\cdots NH_2\cdots NH_2\cdots N$$

followed by the release of a hydrazine molecule. Decomposition of the formed metallic product would give salicylaldehyde azine. Interestingly, the reported chromium and molybdenum complexes did not undergo such catalytic process probably due to their higher stability. It was previously found that when VCl_3(THF), was treated at 20°C in methanol with salicylaldehyde azine and excess of hydrazine yielded the complex $V(sh)_3$.[13] It was also found that when a 2 : 1 stoichiometric ratio of hydrazine to V(salen) complex was used in preparation, salicylaldehyde azine was produced. It was concluded that hydrazine under sufficiently vigorous conditions was able to introduce an $=N{-}N=$ or $-N{-}NH_2$ group for the central $=N{-}CH_2{-}CH_2{-}N=$. In the present reaction, $W(CO)_6$ undoubtedly

Table 3. Selected bond lengths (Å) and angles (°) for salicylaldehyde azine.

Bond lengths			
N(27)–N(27)	1.413(4)	N(27)–C(28)	1.282(3)
C(28)–C(13)	1.440(4)	O(34)–C(14)	1.362(3)
C(13)–C(18)	1.398(4)	C(13)–C(14)	1.411(4)
C(14)–C(15)	1.384(4)	C(15)–C(16)	1.361(4)
C(16)–C(17)	1.388(4)	C(17)–C(18)	
C(28)–H(28)	0.971(3)	O(34)–H(34)	1.380(4)
O(35)–H(35)	0.917(3)		0.903(2)
Bond angles			
N(27)–N(27)–(C28)	113.6(3)	N(27)–C(28)–(C13)	122.2(3)
C(28)–C(13)–(C18)	119.2(3)	C(28)–C(13)–(C14)	123.0(3)
C(18)–C(13)–(C14)	117.8(3)	C(14)–C(15)–(C16)	120.8(3)
Torsion angles			
N(27)–N(27)–(C28)–C(13)	179.9(6)	N(27)–C(28)–(C13)–C(18)	176.3(7)
N(27)–C(28)–(C13)–C(14)	−3.6(4)	C(28)–C(13)–(C18)–C(17)	179.2(7)
C(28)–C(13)–(C14)–O(34)	0.0(4)	C(13)–C(18)–(C17)–C(16)	−1.7(4)



Scheme 2.

catalyzed the process of removing a hydrazine molecule from two shH molecules forming salicylaldehyde azine as confirmed from the analysis of the x-ray structure (Fig. 2) and the IR and Raman spectra (Fig. 1) according to Sch. 2.

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Received May 8, 2004
Accepted August 20, 2004