Oxovanadium(IV) complexes of bromo- and methoxy substituted $N^1,N^4$-diarylidene-$S$-methylthiosemicarbazones

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Abstract: Four new oxovanadium(IV) compounds were prepared by template reaction of salicyl-, 5-bromosalicyl- and 3-methoxysalicyl-aldehyde $S$-methylthiosemicarbazones with 2-hydroxy-, 5-bromo-2-hydroxy- and 3-methoxy-2-hydroxy- benzaldehyde in various combinations. The compounds were isolated as stable solid compounds with general formula [VO(L)] and characterized by elemental analysis, conductivity and magnetic measurements, electronic, IR and EPR spectroscopy. The X-band EPR signals recorded from powder forms of all samples have a single asymmetric line shape and theoretical fit studies proved the presence of axial symmetry around the paramagnetic vanadium ions. The anisotropic Lande splitting factors take values of $g _|| < g _\perp < g _e = 2.0023$. Orbital energy levels for magnetic electrons were determined from theoretically well fitted Spin Hamiltonian parameters. The EPR spectra recorded from solution forms almost have isotropic character.

Keywords: Thiosemicarbazone, $S$-methylthiosemicarbazone, template condensation, EPR, Vanadium

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1 Introduction

Thiosemicarbazones are of considerable interest due to their antitumor, antibacterial, and antiviral activities [1–5]. The biological activities of thiosemicarbazones are considered to be due to substituent effect on aromatic aldehyde/ketone ring and the ability to form chelates with trace metals [6].

The coordination chemistry of vanadium has received considerable attention since discovery of its biological importance, including potent cytotoxic activity against human cancer cells [7], inhibition apoptosis in malignant glioma cells [8], antiamoebic activity [9], antitumor and antiviral activity [10, 11]. Scientists have also tried some of vanadium(IV) compounds on diabetics. Over 150 million people suffer from diabetes mellitus in the world [12–16].

The ability to substitute vanadyl ions instead of spectroscopically silent divalent cations (such as zinc(II), calcium(II) and magnesium(II)) has led to increased usage of vanadyl ions, VO$^{2+}$, as a spectroscopic probe of biological systems by using paramagnetic spectroscopic techniques such as electron paramagnetic resonance (EPR) and electron spin echo envelope modulation (ESEEM) [17]. EPR studies give important knowledge about square pyramidal structure, symmetry, and magnetic properties of oxovanadium(IV) complexes [18, 19].

We report the synthesis and properties of four new oxovanadium(IV) complexes with the formula [(VO)L]. Biological activity must not be mentioned since tests were not performed. The compounds were prepared by reaction of salicyl-, 5-bromosalicyl- and 3-methoxysalicylaldehyde S-methylthiosemicarbazones with 2-hydroxy-, 5-bromo-2-hydroxy- and 3-methoxy-2-hydroxy-benzaldehydes in various combinations, in the presence of VOSO$_4$ (Fig. 1). The compounds were identified by elemental analysis, molar conductivity, magnetic susceptibility, electronic, infrared and electron paramagnetic resonance (EPR) spectroscopies.

![Fig. 1](image)

**Fig. 1** $R_1/R_2$: H/5-Br ($L_i^{IV}$); 5-Br/H ($L_i^{V}$); H/3-OCH$_3$($L_i^{VI}$); 3-OCH$_3$/H ($L_i^{VII}$).
2 Results and discussion

2.1 Some physical properties of the compounds

The thiosemicarbazone ligands, $L_{I-III}$, are crystals which are yellowish in color. The metal complexes form as crystallized powder or a mixture of amorphous and crystal materials. All of the metal complexes are very soluble in DMF and DMSO, while their solubility in ethanol and dichloromethane are poor. Some physical characteristics and analytical data of the template complexes are shown in Table 1.

| Compound       | Colour     | m.p. (°C) | Yield (%) | $R_f$ (CHCl$_3$) | $\lambda_{(M)}$ | $\mu_{eff}$ (B.M.) | Elemental Analysis (%) | Found (Calculated) |
|----------------|------------|-----------|-----------|------------------|----------------|---------------------|-----------------------|-------------------|
| [VO($L_{II}^I$)] | Red-brown  | >390      | 60        | 0.57             | 15.2           | 1.57                | (42.03)               | (2.63) (9.19) (11.15) |
| [VO($L_{II}^I$)] | yellowish green | >390       | 52        | 0.59             | 20.0           | 1.59                | (42.03)               | (2.63) (9.19) (11.15) |
| [VO($L_{III}^I$)] | Light brown | 300-301   | 46        | 0.16             | 16.9           | 1.66                | (50.01)               | (3.68) (10.29) (12.49) |
| [VO($L_{III}^I$)] | Light brown | 309-310   | 43        | 0.18             | 19.4           | 1.64                | (50.01)               | (3.68) (10.29) (12.49) |

$\lambda_{(M)}$: Molar conductivity in DMF at 25±1 °C (Ω$^{-1}$cm$^2$mol$^{-1}$), $\mu_{eff}$: Magnetic susceptibility, $R_f$: Retention factor, m.p. melting point.

Table 1 Physical characteristics and analytical data of the metal compounds.

Elemental analysis show that the interaction of S-methylthiosemicarbazones and the substituted aldehydes in the presence of VO$^{2+}$ in 1:1:1 molar ratio yielded stable solid complexes of the general formula [VO($L$)].

The molar conductivities of the complexes are between 15.2 and 20.0 Ω$^{-1}$cm$^2$ mol$^{-1}$. The values indicate non-ionic character of the complexes.

The $\mu_{eff}$ values are between 1.57 B.M. and 1.66 B.M. The results of the magnetic susceptibility measurements at room temperature showed that complexes were paramagnetic, confirming that the vanadium ions are in the V(IV) state.

Rf values of the complexes were calculated by thin layer chromatography(TLC). TLC was performed on pre-coated silicagel 60 F$_{254}$ TLC plates(Merck), and eluted with CHCl$_3$. The plates were spotted with the complexes and placed in a chromatography tank with lid and the eluent. After the plates were run and the complexes moved, Rf values were determined. The Rf values were defined as the ratio between the distance of spot moved and the distance of solvent moved. This value is dependent on the polarity of the compound and the polarity of the developing solvent. The calculated Rf results were given in Table 1.
2.2 Electronic spectra

The electronic spectra of the ligands in CHCl$_3$ and DMF indicate that each of them has two absorption ($\lambda_1$, $\lambda_2$) of the $\pi \rightarrow \pi^*$, $n \rightarrow \pi^*$ transition. The bands are assignable to the phenyl rings in 307 nm (for L$_I$), 313 nm (for L$_{II}$) and 248 nm (for L$_{III}$), assignable to the thioamide moiety in 337 nm (for L$_I$), 345 nm (for L$_{II}$) and 312 nm (for L$_{III}$).

The electronic spectra of the complexes recorded in CHCl$_3$ and DMF show the same pattern and the $\lambda_{\text{max}}$ values of the bands are shifted only ca. 0–4 nm. The charge transfer bands which can be assigned $\pi \rightarrow \pi^*$ and $n \rightarrow \pi^*$ transitions associated with the thiosemicarbazone moiety and aromatic rings appear in the 242–267 and 317-384 nm regions. In addition, the spectra of each complex display three $d-d$ bands in the 422–444, 631–650 and 953–960 nm regions. These bands may be assigned to the $b_2(d_{xy}, d_{xz}) \rightarrow a_1^*(d_{xy})$, $b_2(d_{x^2-y^2}) \rightarrow e_2^*(d_{xz}, d_{yz})$ and $a_1^*(d_{xy}) \rightarrow e_2^*(d_{xz}, d_{yz})$ transitions, respectively (Table 2). The result indicates a five-coordinate square pyramidal geometry [20–22].

| Complex     | Solvent | Charge transfer | $d-d$ transitions |
|-------------|---------|-----------------|-------------------|
| [VO(L$_I^{II}$)] | CHCl$_3$ | 242 | 319 | 439 | 643 | 956 |
|             | DMF     | 246 | 320 | 438 | 646 | 957 |
| [VO(L$_{II}^{II}$)] | CHCl$_3$ | 240 | 324 | 433 | 633 | 964 |
|             | DMF     | 244 | 328 | 432 | 636 | 960 |
| [VO(L$_{III}^{II}$)] | CHCl$_3$ | 244 | 317 | 433 | 640 | 958 |
|             | DMF     | 246 | 317 | 432 | 642 | 960 |
| [VO(L$_{III}^{II}$)] | CHCl$_3$ | 248 | 384 | 434 | 637 | 953 |
|             | DMF     | 248 | 386 | 432 | 639 | 955 |

Table 2 Electronic spectral data for vanadium(IV) complexes ($\lambda$,nm).

2.3 IR spectra

In the IR spectra of the S-Methylthiosemicarbazones (L$_{I-III}$), there are two sharp bands in the region 3450–3300 cm$^{-1}$ corresponding to the NH$_2$ group, and one band in the region 3150–3050 cm$^{-1}$ which belongs to the OH group. The $\nu$(NH$_2$) bands disappear in the infrared spectra of the complexes because of template condensation. In addition, $\nu$(OH) bands in the spectra of complexes were not recorded due to coordination of the ligand to the metal atom through the deprotonated oxygen atoms of phenolic hydroxyl groups.

In the spectra of L$_{I-III}$, the $\nu$(C=N$^1$) and $\nu$(N$^2$=C) bands were recorded as shoulders of the $\delta$(NH$_2$) band that is a sharp peak between 1651–1601 cm$^{-1}$. As soon as the complexes form, $\delta$(NH$_2$) bands disappear and the $\nu$(C=N) bands of the new conjugated backbone are observed in lower energies by ca. 25 cm$^{-1}$. The spectra of the complexes contain two separated sharp bands in the 1603 ± 5 cm$^{-1}$ and 1581 ± 4 cm$^{-1}$region attributable to $\nu$(C=N$^1$) and $\nu$(N$^4$=C), respectively (see Fig. 1, Table 3).
In addition, the bands belonging to $\nu$(V=O), $\nu$(V-O) and $\nu$(V-N) could be tentatively assigned in the regions 985–981, 461–423 and 519–488 cm$^{-1}$, respectively [23].

| Compound       | $\nu$(C=N$^1$) | $\nu$(N$^2$=C) | $\nu$(C-O)$_{arom}$ | $\nu$(V=O) | $\nu$(V-O) | $\nu$(V-N) |
|---------------|---------------|---------------|-----------------|-----------|-----------|-----------|
| [VO(L$^I_{II}$)] | 1605s         | 1585s         | 1158s           | 985s      | 461w      | 519m      |
|               |               |               | 1131s           |           | 423w      | 496m      |
| [VO(L$^I_{II}$)] | 1605s         | 1578s         | 1146s           | 985s      | 453w      | 511m      |
|               |               |               | 1127s           |           | 426w      | 500sh     |
| [VO(L$^I_{III}$)] | 1608s         | 1582s         | 1158s           | 981s      | 438w      | 515m      |
|               |               |               | 1146sh          |           | 426w      | 496m      |
| [VO(L$^I_{III}$)] | 1597s         | 1578s         | 1162m           | 985s      | 453w      | 500m      |
|               |               |               | 1146s           |           | 438w      | 488m      |

(*) $\nu$: stretching vibration, sh: shoulder, s: sharp, m: medium, w: weak.

Table 3 IR spectral data for the oxovanadium(IV) complexes (KBr Disk, cm$^{-1}$).

2.4 EPR spectra

The room temperature EPR spectra registered for powder and solution forms of all complexes are shown in Figure 2(a–d). The signals registered for powder forms have a single and asymmetric line shape without hyperfine peaks. That is, the negative side of the peaks is wider and of lower amplitude. When we compare these peaks with other EPR signals as given in the literature [24, 25], the origin of paramagnetic peaks must be oxovanadium(IV) ion. The theoretical analyses have proved the presence of dipolar interactions ($\delta a$) [26] in addition to anisotropic Zeeman interaction. The EPR peaks registered for each powder sample indicate axially symmetric character. Their calculated $g_\parallel$ and $g_\perp$ (that can be seen in Table 4 with corresponding $W_\parallel$ and $W_\perp$ line width parameters) values are typical of oxovanadium(IV) systems [25] and lower than the free electron ($g_e = 2.0023$) value as expected for 3d$^1$-system. This case is related to the spin orbit interaction of the ground state with a low-lying excited state [27].

The lone d electron is in a $\sigma$-non-bonding orbital, which points away from the ligands in the xy plane. In the EPR spectra of the samples, nitrogen super-hyperfine splitting is not observed, which indicates that the unpaired electron is located mainly in the $d_{xy}$ orbital. In axially symmetric case of vanadium ion, the same trend is valid for $g_\parallel < g_\perp < g_e$ [28, 29].

The spectra registered for each chloroform solution form include 8 hyperfine lines due to the interaction between nuclear spin of vanadium (I=7/2) ion and electronic spin of magnetic electron. Molecular tumbling effects are observed in the line width character of spectra. Nevertheless, it can be said that the signals recorded from solution forms for each complex have almost isotropic $g_0$ and $a_0$ values. But there are small variations at two adjacent peak separation of hyperfine lines due to second order effects [25, 26].

The amplitude and line width adjustment of peaks have been obtained by the equation
Fig. 2 The room temperature EPR spectra taken from powder and solution forms of (a) [VO(L\text{I}^I)], (b) [VO(L\text{I}^I)], (c) [VO(L\text{I}^I)] and (d) [VO(L\text{I}^I)].

\[ LW = a + b(m_I) + c(m_I)^2 \] [30], where a, b, c are line width coefficients, \( m_I = -I, -I+1, \ldots, -1+I, +I \). The theoretically best fitted \( g_0 \) and line width parameters are given in Table 4.

When we consider the spectra recorded for powder forms, the reason of unresolved hyperfine lines must be the line broadening effects due to the dipolar interactions between neighboring molecules. In the solution, the separation between adjacent molecules increases and dipolar effects get weaker, so hyperfine lines are observed.

The theoretically calculated Spin-Hamiltonian \( g \) and \( A \) values are typical of VO\(^{2+}\) in thiosemicarbazone complexes as in ref.[27–28] The results are found to be in good agreement with the values generally observed for a vanadyl complex with square pyramidal geometry.

As an interesting result, EPR data of four oxovanadium(IV) template compounds show two different behaviors of the d electron of vanadium atom. According to the data, there are basic differences between bromo and methoxy-substituted template systems.
Sample | Powder Forms | Solution Forms
|---|---|---|
| | $g_0$ | $g_{\perp}$ | $g_{\parallel}$ | $\delta a$ (G) | $W_{\perp}$ (G) | $W_{\parallel}$ (G) | $g_0$ | $a_0$ (G) | $a$ (G) | $b$ (G) | $c$ (G)
| VO($L^{II}$) | 1.990 | 1.993 | 1.985 | 30 | 120 | 100 | 1.995 | 102 | 12 | -0.9 | 1.15
| VO($L^{I}$) | 1.992 | 1.996 | 1.985 | 30 | 200 | 140 | 2.001 | 98 | 13 | -0.7 | 1.25
| VO($L^{I}$) | 1.998 | 2.000 | 1.995 | 30 | 250 | 185 | 1.997 | 98 | 14 | -1.5 | 1.0
| VO($L^{I}$) | 1.996 | 1.996 | 1.995 | 30 | 160 | 100 | 1.998 | 98 | 14 | -0.5 | 1.42

(*)The isotropic $g_0$ parameters of axially symmetric EPR signals for powder forms, have been calculated by the equation $g_0 = \frac{g_\parallel + 2g_\perp}{3}$ [25].

Table 4 EPR and line width parameters obtained from theoretical calculations.

Some of physical properties such as melting point and $R_f$ value confirm these two formations (Table 1). It can be observed a correlation even between colors and hyperfine features of the compounds. While VO($L^{II}$) and VO($L^{I}$) have the same colors and quite similar hyperfine lines, VO($L^{I}$) and VO($L^{I}$) are in different colors and give partially similar EPR spectra. In addition, the difference between the hyperfine lines indicates that the dynamic behavior (rotation) of two groups in chloroform solution is different.

In conclusion, it was become evident that the substituent (bromo or methoxy) on aromatic ring specified the electron behavior of oxovanadium(IV) ion in the template compounds. The structural determination studies related to other substituents of oxovanadium(IV) templates are in progress.

3 Experimental

3.1 Materials, methods and apparatus

All chemicals and solvents were of reagent grade. IR spectra were recorded (KBr disks) on a Mattson 1000 FT-IR spectrometer. The elemental analyses were determined on a Carlo- Erba 1106 Elemental Analyser. The vanadium content was determined complexometrically [31]. $^1$H-NMR spectra were obtained on a Bruker AC-200 NMR spectrometer (Tubitak, Turkey). UV-Vis spectra were recorded ATI-Unicam UV/visible-UV2 spectrophotometer. Molar conductivities of $10^{-3}$ M DMF solutions were measured at $25 \pm 1 \, ^\circ\text{C}$ using a digital CMD 750 conductivity meter. Magnetic measurements were carried out at room temperature by the Gouy technique with an MK I model device obtained from Sherwood Scientific. The room temperature EPR spectra for powder and chloroform solution forms have been registered by a conventional X-band ($\nu = 9.5 - 9.8 \, \text{GHz}$) Bruker EMX model spectrometer employing an ac magnetic modulation technique.
4 Synthesis of ligands and complexes

4.1 S-Methylthiosemicarbazones (L$_{I-III}$)

S-methylthiosemicarbazones of 2-hydroxy- (L$_I$), 5-bromo-2-hydroxy- (L$_{II}$) and 3-methoxy-2-hydroxy- (L$_{III}$) benzaldehyde were prepared according to the literature [1,3], and characterized by melting points and spectral data. The colours, melting points, yields, $^1$H-NMR and IR data of L$_{I-III}$ were given as follows:

L$_I$: light yellow, 160-161 °C, 97%, $^1$H-NMR (DMSO-d$_6$, 25 °C, ppm): δ 11.58, 10.83 (cis/trans ratio: 3/2, s, 1H, CH=NH), δ 6.94 (s, 2H, NH$_2$), δ 7.59, 7.39 (d-d, J:7.44, 1H, d), 7.24 (t, J:7.63, J:7.84, 1H, b), 6.90 (t, J:7.50, J:7.61 1H, c), 6.87 (s, 1H, a), 2.43, 2.40 (cis/trans ratio: 3/2, s, 3H, S-CH$_3$), FT-IR (KBr, cm$^{-1}$): ν$_a$(NH) 3457, ν$_s$(NH) 3280, ν(OH) 3052, δ(NH) 1635, ν(C=N$_1$), ν(N$_2$=C) 1616, 1605, ν(C-O) 1150.

L$_{II}$: yellow, 198-199 °C, 91%, $^1$H-NMR (DMSO-d$_6$, 25 °C, ppm): δ 11.65, 10.79 (cis/trans ratio: 3/2, s, 1H, OH), δ 6.34, 8.33 (syn/anti ratio: 2/3, s, 1H, CH=NH$_1$), δ 7.00 (s, 2H, NH$_2$), 7.64 (d-d, J:2.52, 1H, d), 7.35 (m, 1H, b), 6.87-6.85 (d-d, J:1.52, 1H, a), 2.44, 2.39 (cis/trans ratio: 3/2, s, 3H, S-CH$_3$), FT-IR (KBr, cm$^{-1}$): ν$_a$(NH) 3476, ν$_s$(NH) 3276, ν(OH) 3084, δ(NH) 1632, ν(C=N$_1$), ν(N$_2$=C) 1620, 1607, ν(C-O) 1153.

L$_{III}$: cream, 164-165 °C, 93%, $^1$H-NMR (DMSO-d$_6$, 25 °C, ppm): δ 11.58, 10.71 (cis/trans ratio: 2/1, s, 1H, OH), δ 8.44, 8.30 (syn/anti ratio: 2/3, s, 1H, CH=NH$_1$), δ 6.84 (s, 2H, NH$_2$), 7.14-6.99 (d-d, J:7.43, J:1.25, 1H, d), 6.80 (t, 1H, J:8.04, c), 6.94 (d, J:6.92, 1H, b), 2.42, 2.37 (cis/trans ratio: 3/2, s, 3H, S-CH$_3$), δ 3.77 (s, 3H, OCH$_3$), FT-IR (KBr, cm$^{-1}$): ν$_a$(NH) 3412, ν$_s$(NH) 3306, ν(OH) 3129, δ(NH) 1651, ν(C=N$_1$), ν(N$_2$=C) 1628, 1601, ν(C-O) 1154.

4.2 N$_1$-salicylidene-N$_4$-5-bromosalicylidene-S-methylthiosemicarbazidato-oxovanadium(IV) [VO(L$_{II}$)]

Salicylaldehyde-S-methylthiosemicarbazone (1 g, 1 mmol) and 5-bromosalicylaldehyde (0.96 g, 1 mmol) were dissolved in ethanol (25 cm$^3$). The solution was then added by stirring to a solution of 1.21 g (1 mmol) VOSO$_4$·5H$_2$O and triethylortoformate (ca. 5.5 cm$^3$) in ethanol (25 cm$^3$). After 1 h at room temperature, triethylamine (ca. 8.5 cm$^3$) was added into the reaction mixture. After 48 h, the precipitated yellowishgreen crystals were filtered off, washed with ethanol-ether (1:1, 10 cm$^3$) and dried in vacuo over P$_2$O$_5$ (yield 1.31 g, 60%).

The oxovanadium(IV) complexes with L$_{II}$, L$_{II}$ and L$_{III}$ systems were prepared in similar manner.
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