

Synthesis and Spectroscopic Characterization of Oxalyl Bis(Diacetylmonoxime Hydrazone) Metal Complexes

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ABSTRACT: Binuclear complexes of VO²⁺, Co²⁺, Ni²⁺, Cu²⁺ and Zn²⁺ with oxalyl bis(diacetylmonoxime hydrazone), H₄ODMH, have been prepared. Elemental analysis, spectral studies (IR, U.V-Vis., ¹H NMR, ESR, MS) and magnetic measurements were proved the structure of the formed chelates. The data of elemental analysis suggest a 2:2 (M:L) molar ratio. H₄ODMH behaves as a dibasic tetradentate ligand in all the studied complexes. The electronic spectra and magnetic moments reveal an octahedral geometry for the VO²⁺ complex, tetrahedral for the Zn(II) and square-planar for the rest. The anomalous magnetic moment for the VO²⁺ complex is taken as strong evidence for the metal-metal bond. The ESR spectra of the Cu(II) complex, in powder and DMF solution, reveal a square-planar geometry. The *in vitro* antimicrobial activity of the investigated compounds reveals a higher activity of H₄ODMH than its complexes.

Key words: Metal Complexes, Oxalyl Bis (Diacetylmonoxime Hydrazone), Spectroscopic Characterization, antimicrobial activity.

Introduction

Recently, a great interest is focused on the synthesis and structural characterization of transition metal chelates of hydrazone derivatives to compare their coordinative behavior with their antimicrobial activities. It was mentioned that certain hydrazones and their Cu(II) complexes have antitumor activity [1]. Diacetyl monoxime thiosemicarbazone is effective against vaccinia infections in mice and may act by removing some essential metal ions from the vaccinia virus by

chelation [2]. Oximinohydrazones have antiparasitic, fungicidal and bactericidal properties [3]. Compounds containing oxime and amino groups are used as analytical reagents for the microdetermination of some transition metal ions and as ion exchange resins [4]. Previous papers [5-11] were reported on the synthesis and characterization of some oxime hydrazone complexes.

Experimental

Co(NO₃)₂·6H₂O, Ni(NO₃)₂·6H₂O, Cu(NO₃)₂·2.5H₂O, H₂PtCl₆, VOSO₄·2H₂O, diethyl oxalate, hydrazine hydrate, diacetylmonoxime, ethanol, diethyl ether, DMF and DMSO were obtained from BDH, Sigma or Merck.

Synthesis of H₄ODMH

Oxalyl bis(diacetylmonoxime hydrazone), Fig. 1, was prepared by condensing a suspension (6 g, 0.1mol) of oxalic acid dihydrazide (NH₂NHCOCONHNH₂) in 20 mL EtOH with 20 g (0.2mol) of diacetylmonoxime in 10 mL EtOH. The reaction mixture was heated under reflux on a water bath for one day till completion of the reaction (tested using TLC). The precipitate was filtered off, recrystallized from ethanol and dried. The ligand was

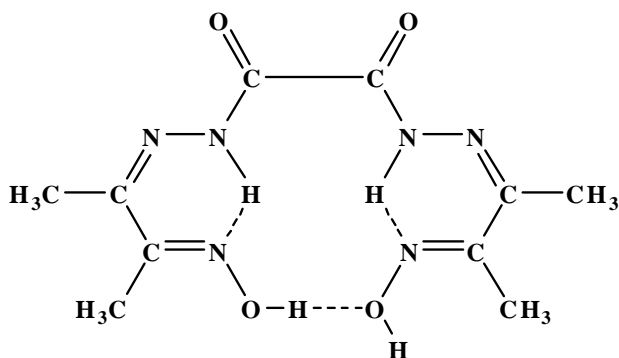


Figure 1: Structure of H₄ODMH

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characterized by spectral (IR and ^1H NMR) studies and elemental analysis.

The IR spectrum of the ligand shows bands at 3390(w), 3295(w), 3183(w), 1695(vs), 1610(s), 1560(w), 1506(vs), 1274(s) and 998(vs) due to $\nu(\text{OH})_{\text{free}}$, $\nu(\text{OH})_{\text{bonded}}$, $\nu(\text{NH})$, $\nu(\text{C}=\text{O})$, $\nu(\text{C}=\text{N}_{\text{hydrazone}})$, $\nu(\text{C}=\text{N}_{\text{oxime}})$, $\nu(\text{OH})$ and $\nu(\text{NO})$, respectively. The spectrum also shows another broad bands at 1860 and 2800 cm^{-1} which may be due to N-H...N or O-H...O hydrogen bonding (Fig. 1). Its ^1H NMR spectrum shows signals for intramolecular hydrogen bonded OH protons at $\delta = 11.5$ (s, 2H); NH at $\delta = 11.35$ (s, 2H) as well as the four methyl groups at $\delta = 3.33$ (s, 6H) and $\delta = 2.53$ (s, 6H).

Preparation of complexes

The solid complexes were prepared by reacting the calculated amounts for 2:1 ratio of both metal salt and ligand in H_2O -EtOH (v/v) solution and the mixture was heated under reflux on a water bath for 4 - 6 h. In the preparation of VO^{2+} complex, 0.1 g of sodium acetate was added. The precipitate thus formed was filtered off, washed with hot water, hot ethanol and diethyl ether and finally dried in a vacuum desiccator over anhydrous CaCl_2 .

Antibacterial and Antifungal Studies

The organic ligand and its metal complexes were screened for their antimicrobial activity using *Azotobacter* as a bacteria and *Aspergillus Niger* as a fungus. The media prepared for bacteria and fungus were as reported earlier [12].

Equipment and Analysis

Carbon, hydrogen and nitrogen content of the ligand and its complexes was determined at the Microanalytical Unit of Cairo University, Egypt. The metal content was determined complexometrically [13]. The IR spectra were recorded as KBr disc on a Mattson 5000 FTIR Spectrophotometer. The UV-Vis. spectra of the complexes were recorded on UV₂ Unicam Spectrophotometer. The ^1H NMR spectra, in $d_6\text{DMSO}$, were recorded on a Varian Gemini Spectrophotometer (200 MHz). The ESR spectra of the Cu(II) complex (DMF solution and powder) at 300 K were recorded on a Bruker EMX Spectrometer working in the X- band (9.78 MHz) with 100 KHz modulation frequency, 1mw microwave power and 4G modulation amplitude. The magnetic measurements were carried out on a Johnson-Matthey magnetic balance, UK. The effective magnetic

moments were evaluated by applying: $m_{\text{eff}}: 2.828 \sqrt{\chi_M T}$,

where χ_M is the molar susceptibility corrected using Pascal's constants for the diamagnetism of all atoms in the ligand. Thermogravimetry was measured (20-1000 $^\circ\text{C}$) on a Shimadzu (TGA-50). The nitrogen flow and heating rate were 20 ml min^{-1} and 10 $^\circ\text{C min}^{-1}$, respectively.

Results and Discussion

The data of elemental analysis together with the physical properties of H_4ODMH and its complexes are summarized in *Table 1*. The results confirm the general formula $[\text{M}_2(\text{H}_2\text{ODMH})_2]$ for all the isolated complexes. The magnetic susceptibilities of the complexes are consistent with values corresponding to those reported for a square-planar geometry around the central metal ions. The subnormal values may be due to metal-metal interaction; the lower the value the strong the interaction. The VO^{2+} complex shows zero moment due to V-V bond. The thermal analysis confirms higher stability for the Co(II), Zn(II) and VO^{2+} complexes till 249, 150 and 153 $^\circ\text{C}$. The partial solubility of the complexes in DMSO and/or DMF prevents their conductance measurements.

IR Spectra

The IR spectrum (*Table 2*) of H_4ODMH shows three bands at 3390, 3295 and 1274 cm^{-1} assigned to the stretching and bending vibrations of the OH groups. The stretching bands appear as doublet and at lower wavenumbers which may be due to intramolecular hydrogen bonding [14]; the lower the values the strong the hydrogen bonding (*Fig. 1*). The absence of these bands in the spectra of the complexes indicates the deprotonation of the OH groups during complexation. The bands due to $\nu(\text{C}=\text{N}_{\text{hydrazone}})$ and $\nu(\text{C}=\text{N}_{\text{oxime}})$ appeared at low frequency in the complex spectrum and overlapping with each other in the 1590-1506 region indicating their participation in chelation.

More or less unshift for the $\nu(\text{NO})$ band (at ca. 1000 cm^{-1}) may be due to the covalent attachment of its nitrogen in chelation after disappearance of the hydrogen bonding. The $\nu(\text{C}=\text{O})$ and $\nu(\text{NH})$ bands are unaffected; this is a characteristic feature for their uncoordination. Also, the IR. spectra of the metal chelates show new bands in the 420-480 cm^{-1} region probably due to $\nu(\text{M}-\text{N})$ [15]. In addition, the vanadyl complex shows a broad band centered at 1000 cm^{-1} attributed to $\nu(\text{V}=\text{O})$ which is a former evidence for the octahedral configuration of

Table 1
Analytical and physical data of H₄ODMH and its metal complexes

Compound	Color	%Found (calcd)				M.Wt, Found (calcd.)
		C	H	N	M	
(1) H ₄ ODMH	White	42.1 (42.3)	5.6 (5.7)	-	-	-(284.4)
(2) [Co(H ₂ ODMH)] ₂	Yellow	35.6 (35.2)	4.4 (4.1)	24.1 (24.6)	17.1 (17.3)	-(682.4)
(3) [Cu(H ₂ ODMH)] ₂	Brown	34.3 (34.7)	4.2 (4.1)	24.3 (24.3)	18.7 (18.4)	690 (691.7)
(4) [Ni(H ₂ ODMH)] ₂	Yellow	35.2 (35.2)	3.9 (4.1)	24.6 (24.6)	17.6 (17.2)	681 (682.1)
(5) [Zn(H ₂ ODMH)] ₂	White	34.6 (34.5)	4.5 (4.1)	-	18.3 (18.7)	-(695.5)
(6) [VO(H ₂ ODMH)] ₂	Gray	34.6 (34.4)	4.5 (4.0)	24.3 (24.1)	14.1 (14.6)	-(698.6)

Table 2
IR spectral bands (cm⁻¹) of H₄ODMH and its metal complexes

Compound	$\nu(N^1H)$	$\nu(N^2H)$	$\nu(OH)$	$\nu(C=O)$	$\nu(C=N_{\text{hydrazone}})$	$\nu(C=N_{\text{oxime}})$	amide (II)	$\nu(NOH)$	$\nu(M-N)$
(1)	3390(s)	3295(s)	3183(m)	1700(vs)	1610(m)	1590(w)	1506(vs)	998(vs)	-
(2)	3394(s)	3305(s)	-	1700(vs)	1506(vs)	-	-	1000(s)	420(m)
(3)	3392(s)	3305(s)	-	1695(vs)	1579(m)	1508(vs)	-	1000(s)	440(w)
(4)	3392(s)	3305(m)	-	1695(vs)	1508(vs)	1506(s)	1506(vs)	1000(s)	425(m)
(5)	3392(s)	3303(s)	-	1695(vs)	-	-	-	998(s)	440(m)
(6)	3396(s)	3305(s)	-	1697(vs)	-	-	-	1000(vs)	42(m)

vs=very strong; s=strong; m=medium; w=weak

the VO²⁺ complex [16]. The broadness of the band may be due to its overlapping with $\nu(NO)$.

Electronic and magnetic studies

The electronic spectra of the complexes as well as the magnetic moment values (Table 3) offer a good evidence for variable structures. Square-planar geometry is proposed for [Co(H₂ODMH)]₂, [Ni(H₂ODMH)]₂ and [Cu(H₂ODMH)]₂. This is based on the data abstracted from their electronic spectra in DMSO and verified by the conformity with Nujol mull. The bands at 19080 and 19050 cm⁻¹ in the Co(II) and Ni(II) complexes are assigned to the ²B_{2g} → ²A_{1g} and ¹A_{1g} → ²A_{2g} transitions [17]. In addition, the spectrum of the Cu(II) complex shows two bands at 16780 and 14280 cm⁻¹ which are assigned to the ²B_{1g} → ²E_g and ²B_{1g} → ²A_{1g} transitions [18]. These bands suggest a square-planar geometry for the three complexes. The diamagnetic value of the Ni(II) complex (Table 3) agrees with the proposed geometry. However, the subnormal magnetic moments of the Co(II) and Cu(II) chelates reflect a behaviour for the binuclear complexes representing in a strong metal-metal interaction. The color (Table 1) characterized such complexes is a further confirmation for the square-planar configuration. The presence of two bands at 22370 and 19180 cm⁻¹ in [VO(H₄ODMH)]₂ are assigned to the ²B₂ → ²E (n₁) and

²B₂ → ²B₁ (n₂) transitions [19], respectively, supports an octahedral geometry. Its diamagnetic character offers a strong evidence for the presence of V-V bond in dimeric form (Fig. 2). Representative elucidation of its geometry as well as the Cu(II) complex in the three dimensions is in agreement with the suggested structure.

Table 3
Magnetic Moments (B.M) and Electronic Spectral Bands (cm⁻¹) of the Complexes.

Complex	μ_{eff}	d-d transition	charge transfer	Proposed structure
(2)	1.46	19080	24810	Square-planar
(3)	1.37	16780; 14280	23150	Square-planar
(4)	0.00	19050	24310	square-planar
(6)	0.00	22370; 18180	24330	Octahedral

Thermal analysis

The thermogravimetric analyses at 25-1000 °C for some complexes were recorded to elucidate the coordinated and hydrated solvents and to give insight about the thermal stability of the studied complexes.

The TG and DTG curves of [VO(H₂ODMH)]₂ displayed a thermal stability till 153 °C, after which two degradation steps are observed in the 153-660 °C range. The first decomposition step (153-445 °C) is observed

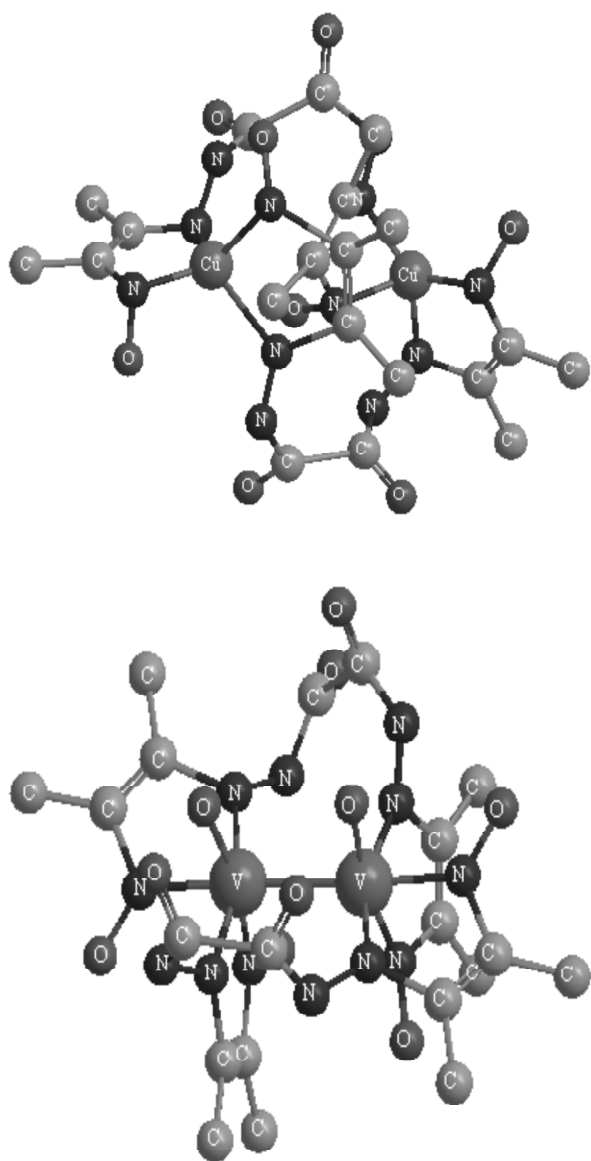
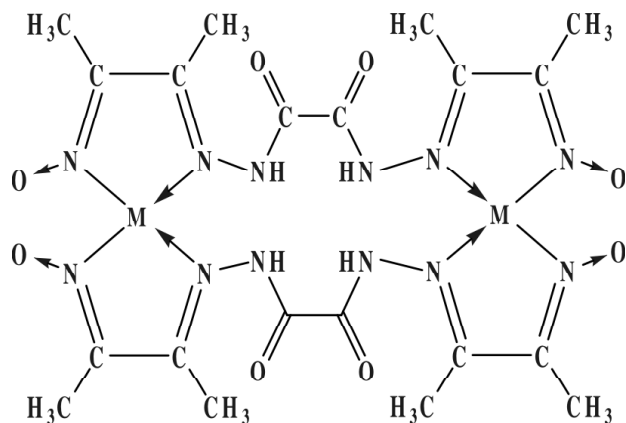


Figure 2: General structures of the complexes

due to the removal of 8CH₃ and 4CO with 34.1% (calcd., 33.2%) weight loss. In the 455-660 °C range, 4NH groups are removed from the organic moiety by 6.9% (8.5%) weight loss. [VO(C₄N₄O₂)₂] (Figure 3 shown below) is the residual part by 59.0% (calcd., 58.5%) which reveal a higher thermal stability of the complex. The existence of this moiety at high temperature may be related to the strong V-V bond.

The curve recorded for [Co(H₂ODMH)]₂ showed a relative stability, which translated to one decomposition step in the 250-255 °C region by 91.8% (calcd 91.4%) weight loss. The Co atom still as a residual part by 8.3% (8.6% calcd.) weight per cent.

The TG curve of [Zn(H₂ODMH)]₂ showed a thermal stability up to 150 °C followed by two decomposition steps. The first decomposition stage at 150-255 °C is attributed to the removal of 8(CH₃) with a weight loss 18.7% (calcd.17.3%). The second at 256-353 °C is major and represents the removal of high moiety (C₁₂H₄N₁₂O₈) with a weight loss of 64.6(calcd., 63.9%) leaving two zinc atoms as a final product with 16.7%(calcd., 18.8%).

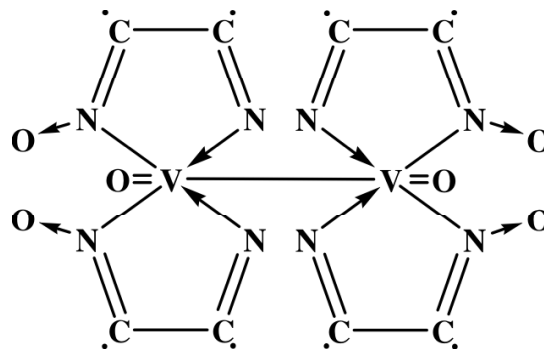


Figure 3: Structure of [VO(C₄N₄O₂)₂]

Mass spectra

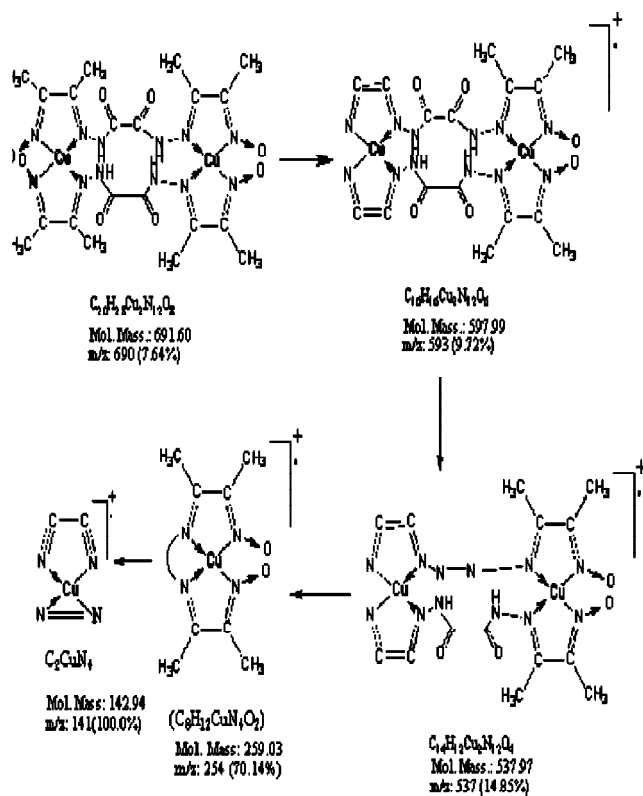
The mass spectra of some investigated complexes provide high confirmation for the suggested formula. The mass spectrum of [Ni(H₂ODMH)]₂ showed multiple peaks representing successive degradation steps of the molecule. The first peak at *m/z* = 681 (calcd. 682.1) represents the molecular ion of the complex with 1.03% abundance. The base peak (100% abundance) with *m/z*=95 represents the final residue (NiO₂).

The mass spectrum of [Cu(H₂ODMH)]₂ showed *m/z* = 691 with 7.6% abundance corresponding to (M+1)⁺ ion peak. Multiple peaks are observed throughout the spectrum. The main peaks with high abundance percent at *m/z*=593(9.7%), 537(14.6%), 421(15.3%), 254(70.2%)

and 141(100%) due to the removal of $4\text{CH}_3 + \text{O}_2$, 2CO , $\text{C}_2\text{H}_4\text{N}_4\text{O}_2$, $\text{C}_4\text{N}_4\text{Cu}$ and $\text{C}_6\text{H}_8\text{O}_2$. CuC_2N_4 is the residual part with $m/z=141$ (100%). The degradation steps may be represented in the following Scheme (1).

Biological activity

The ligand and its metal complexes were screened against *Azotobacter* as bacteria and *Aspergillus Niger* as a fungus. The results are cited in Table 4. The ligand and its complexes have a relative activity towards fungus than bacteria. The comparison between their biological activities is based on comparing the diameter of the inhibition zone (cm). The inhibition zone in case of fungus is higher than that of bacteria. The lower activity of the complexes than the free ligand is a behavior observed from the results. Such activity of the metal chelates may be due to the lipophilic nature of the metal ions in complexes.



The activity in case of fungus decreases in the order: $\text{H}_4\text{ODMH} > \text{Ni(II)} > \text{Cu(II)} > \text{Co(II)} > \text{VO}^{2+} > \text{Zn(II)}$ while in bacteria is as follows: $\text{H}_4\text{DAMOH} > \text{Ni(II)} > \text{Co(II)} > \text{Cu(II)} > \text{Zn(II)} > \text{VO}^{2+}$.

Table 4
The Biological Activity of H_4ODMH and its Complexes

Compound	<i>Aspergillus Niger</i> (%)	<i>Azotobacter</i> (%)
H_4ODMH	53.6	44.6
$[\text{Co}(\text{H}_2\text{ODMH})]_2$	38.3	28.0
$[\text{Cu}(\text{H}_2\text{ODMH})]_2$	33.1	25.5
$[\text{Ni}(\text{H}_2\text{ODMH})]_2$	48.5	42.0
$[\text{Zn}(\text{H}_2\text{ODMH})]_2$	19.1	16.6
$[\text{VO}(\text{H}_2\text{ODMH})]_2$	30.6	15.3

ESR Spectra

The ESR spectrum of the Cu(II) complex was recorded in the solid state to obtain further information about the stereochemistry, the metal-ligand bonding and the magnetic interaction. The spin Hamiltonian parameters were calculated to be: $g_{\parallel} = 2.26$, $g_{\perp} = 2.11$ and $G = 2.25$. The room temperature spectrum exhibits an axially symmetric g-tensor parameters with $g_{\parallel} > g_{\perp} > 2.0023$ indicating $d_{x^2-y^2}$ is the ground-state characteristic of square planar or octahedral stereochemistry [20]. The calculated G value is 2.25 suggesting a copper-copper exchange interaction.

A forbidden magnetic dipolar transition for the Cu(II) complex is also observed at half-field (1600 G) and $g = ca. 4.0$, but the intensity is very weak. The present ESR spectrum is similar to that of the binuclear Cu(II) complexes [21]. The appearance of the half-field signal confirms the binuclear unit and magnetic interaction between the two Cu(II) ions. The spectrum (Fig. 4) is broad single line which attributed to dipolar broadening and enhanced spin lattice relaxation [22]. This line broadening is probably due to insufficient spin-exchange narrowing toward the coalescence of four copper hyperfine lines to a single line, the same kind of powder ESR line shapes, has been observed for many square-planar dimeric copper(II) complexes with considerably strong spin-exchange interaction. [23].

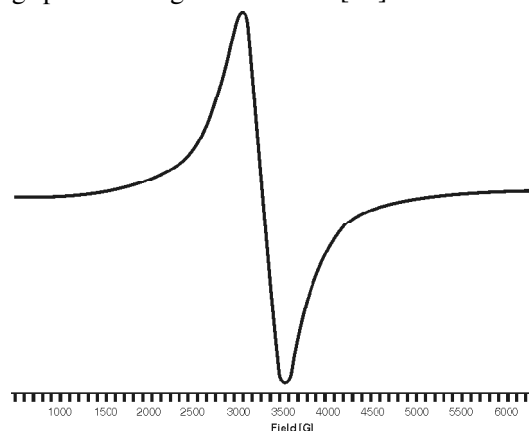


Figure 4: ESR spectrum of Cu(II) complex

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