



Preparation and Spectral Properties of Mixed-Ligand Complexes of VO(IV), Ni(II), Zn(II), Pd(II), Cd(II) and Pb(II) with Dimethylglyoxime and *N*-Acetyl glycine

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Abstract: A number of mixed-ligand complexes of the general formula [M(D)(G)] where D=dimethylglyoximate monoanion, G=*N*-acetyl glycinato and M=VO(IV), Ni(II), Zn(II), Pd(II), Cd(II) and Pb(II) were prepared. Each complex was characterized by elemental analysis, determination of metal, infrared spectra, electronic spectra, (¹H and ¹³C) NMR spectra, conductivity and magnetic moments. All these complexes were not soluble in some of the organic solvent but highly soluble in dimethylformamide. The conductivity data showed the non-electrolytic nature of the complexes. The electronic spectra exhibited absorption bands in the visible region caused by the *d-d* electronic transition such as VO(IV), Ni(II) and Pd(II). The IR and (¹H, ¹³C) NMR spectra which have indicate that the dimethylglyoxime was coordinated with the metal ions through the N and O atoms of the oxime group and *N*-acetyl glycine was coordinated with metal ions through the N atom and terminal carboxyl oxygen atom.

Keywords: Dimethylglyoxime complexes, *N*-acetyl glycine complexes, Mixed ligand complexes, Spectral properties.

Introduction

The dimethylglyoxime derivatives have received considerable attention from both of the chemical and biological scientists. It is stimulated the reactions of vitamin B₁₂ and vitamin- B₁₂

model chemistry¹⁻³. Moreover, the dioximes are capable of coordinating through N, N or N, O sites of the oxime groups. Thus, some of the dioximes derivatives exhibited significant anticarcinogenic activity and antitumor agents¹. The most famous complex among other complexes is the bright red Ni(dmgH)₂. This planer complex is very poorly soluble and is used for the gravimetric determination of nickel^{4,5}. There is lot of work have been done like *trans*-bis(dimethylglyoximato) with metal complexes⁶⁻⁸. Furthermore, the IR spectra of some dimethylglyoxime complexes show the formation of the strong metal-N covalent bonds and the presence of intra molecular O-H-O bonds⁹.

An amino acid like *N*-acetyl glycine has been taken special attention in environment as it contains a peptide bond. The complexing ability towards the transition metal ions has not been extensively investigated¹⁰. Knowing this, the mixed ligand complexes of *N*-acetyl glycine and dimethylglyoxime with some metal ions were prepared and investigated by IR, electronic and ¹H- and ¹³C NMR spectra and magnetic measurements.

Experimental

All chemicals were obtained from commercial sources and were used without further purifications. VOSO₄.H₂O, NiCl₂.6H₂O, ZnCl₂, PdCl₂, CdCl₂.H₂O, Pb(NO₃)₂ and KOH were obtained from Fluka. Dimethylglyoxime and *N*-acetyl glycine from Merck. Methanol, ethanol, dimethylformamide and dimethylglyoxime-*d*₆ from BDH.

UV-Visible spectra were measured in dimethylformamide (DMF) using a Shimadzu UV-Visible recorder spectrophotometer UV-160. The I.R spectra in the range of 4000-400 cm⁻¹ were recorded as potassium bromide disc on a Shimadzu FTIR-8300 Fourier Transform infrared spectrophotometer. Determinations for metals were carried out using gravimetric methods. Elemental analysis (C, H, N) was performed on a perkin Elmer B-240 Elemental Analyzer. ¹H NMR and ¹³C NMR spectra were recorded using the JEOL JNM-ECP 400 Spectrometer in DMSO-*d*₆, relative to the internal standard tetramethylsilane (TMS). Conductivity measurements were carried out at 25 °C in DMF using a Philips Pw-9526 digital conductivity meter. Melting points were determined using a stuart-melting point apparatus and finally the magnetic susceptibility measurements were obtained using a magnetic susceptibility balance, model MsB-MK1.

General procedure for synthesis

An ethanolic KOH solution (12 mL) of dimethylglyoxime (D) (0.17-0.42 g) and an ethanolic KOH solution (10 mL) of *N*-acetyl glycine (G) (0.24-0.42 g) were added respectively to an aqueous solution of metal salts, after constant stirring on water bath. The product precipitates immediately, filtered off and washed three times and recrystallized with 1:3 ethanol: water mixture. Then, it was dried in an oven at 60 °C.

Results and Discussion

The prepared complexes were found to be solids, insoluble in some of the organic solvents such as acetone, acetonitrile and chloroform but completely soluble in dimethylformamide. The lower value of molar conductivity in DMF indicates the non-electrolyte behavior of this complexes¹¹⁻¹³. All the compounds reported in this work are presented in Table 1 along with their analytical data, melting points and conductivity values at room temperature.

Table 1. Analytical and physical data of the prepared complexes

Compound	Color	Yield %	M.P. C°	Elemental Analysis Calc, found%				Molar conductivity Ohm ⁻¹ cm ² mol ⁻¹
				C	H	N	M	
[VO(D)(G)]	Green	60	210-211	32.88 (31.60)	4.48 (4.03)	14.38 (14.10)	17.43 (16.90)	5
[Ni(D)(G)]	Pink	65	>300	33.84 (33.10)	4.61 (3.22)	14.80 (14.40)	20.68 (20.03)	6
[Zn(D)(G)]	Whit	70	>300	33.06 (32.99)	4.50 (3.86)	14.46 (14.02)	22.47 (21.22)	6
[Pd(D)(G)]	Yellow	69	270-272	28.97 (28.55)	3.95 (3.14)	12.67 (12.25)	32.08 (31.61)	5
[Cd(D)(G)]	White	50	>300	28.45 (28.96)	3.88 (2.01)	12.44 (11.98)	33.29 (32.89)	10
[Pb(D)(G)]	White	55	>300	22.22 (21.45)	3.03 (3.76)	9.72 (9.65)	47.91 (46.5)	7

Infrared spectra

The infrared spectra of the dimethylglyoxime exhibited absorption bands at 3400, 2931, 1570, 1141 and 756 cm⁻¹ which are attributed to $\nu(\text{OH})$, $\nu(\text{C-H})$ aliphatic, $\nu(\text{C=N})$, $\nu(\text{N-O})$ and $\nu(\text{C=N-O})$ respectively. In addition, on the complexes the bands of $\nu(\text{C=N})$ and $\nu(\text{C=N-O})$ were shifted to the lower frequencies by 43-6 and 16-6 cm⁻¹. This type of coordination is usual in the complexes, as the ligand forms six-member chelate ring by coordinating with metal ions through the N and O atoms^{1,3,14}. The infrared spectrum of *N*-acetylglycine shows absorption band at 3380 cm⁻¹ which belongs to the $\nu(\text{NH})$. On complexes formation, this band was shifted to the lower frequencies by 159-125 cm⁻¹. Moreover, it is noted that both of the $\nu(\text{COO})$ asymmetric and symmetric bands of the ligand (G) appeared at 1740 and 1370 cm⁻¹. On complexes formation these two bands were shifted to the lower frequencies by 90-43 and 10-5 cm⁻¹ respectively. The $\nu(\text{NH})$ and $\nu(\text{COO})$ bands of the ligand (G) after coordination excluding the coordination of these groups with metal ions were observed^{10,15}. Thus, the spectra of the complexes appear as weak bands between 408-470 and 470-520 cm⁻¹ which are due to the $\nu(\text{M-N})$ and $\nu(\text{M-O})$ respectively. This is indicated that the dimethylglyoxime and *N*-acetylglycine as a bidentate and are coordinated with the metal ions through the N and O atoms. So, the VO(IV) complex exhibited strong and sharp band at 979 cm⁻¹ which is attributed to the $\nu(\text{V=O})$. All the data are listed in Table 2.

Table 2. The infrared spectral data (cm⁻¹) of the free ligands and their complexes

Compound	$\nu(\text{OH})$	$\nu(\text{NH})$	$\nu(\text{COO})_{\text{asy}}$	$\nu(\text{C=N})$	$\nu(\text{COO})_{\text{sy}}$	$\nu(\text{N-O})$	$\nu(\text{C=N-O})$	$\nu(\text{M-O})$	$\delta(\text{M-N})$
D	3400	-	-	1570	-	1141	756	-	-
G	-	3380	1740	-	1370	-	-	-	-
[VO(D)(G)]	3332	3240	1689	1527	1365	1139	750	470	408
[Ni(D)(G)]	3425	3255	1689	1566	1365	1103	748	516	424
[Zn(D)(G)]	3450	3232	1650	1550	1360	1135	750	520	470
[Pd(D)(G)]	3420	3209	1689	1540	1360	1135	750	470	408
[Cd(D)(G)]	3517	3217	1670	1560	1363	1130	740	470	416
[Pb(D)(G)]	3549	3201	1697	1550	1362	1130	750	470	420

¹H NMR spectra

The ¹H NMR spectra show single signal at 1.90 ppm which is attributed to the methyl groups of the dimethylglyoxime ligand. This peak undergoes a downfield shifted in the complexes by 0.30-0.40 ppm. In general, downfield shifts observed on chelation may be due to the decrease in electron density which is caused by ligand interaction with the metal ions^{2,16}. The δ due to the OH proton in ligand D appears at 11.20 ppm. This signal is shifted downfield in the complexes which appeared between 11.36-11.42 ppm. Upon coordination of the metal ions with the nitrogen atom of the C=N group and the oxygen of the C=N-O^{2,17,18}.

The *N*-acetyl glycine shows single signal at 2.08 ppm which is attributed to the methyl group. Moreover, the spectrum of the ligand appeared two singlet signals at 6.35 and 4.03 ppm which are caused by the NH and CH₂ groups respectively. In complexes the signal due to the NH group was shifted downfield by 15-20 ppm. Nevertheless, the signal of the CH₂ group was shifted upfield by 0.64-0.23 ppm¹⁹. Table 3 summarizes the ¹H NMR data for the free ligands and their complexes in DMSO-*d*₆.

Table 3. ¹H NMR chemical shifts (δ, ppm) of the free ligands and their complexes

Compound	OH _D	CH ₃ _D	NH _G	CH ₂ _G	CH ₃ _G
D	11.20	1.90	-	-	-
G	-	-	6.35	4.03	2.08
[Ni(D)(G)]	11.40	2.20	6.50	3.56	2.0
[Zn(D)(G)]	11.41	2.25	6.50	3.6	2.1
[Pd(D)(G)]	11.37	2.30	6.52	3.8	2.06
[Cd(D)(G)]	11.36	2.30	6.55	3.51	2.06
[Pb(D)(G)]	11.42	2.21	6.55	3.39	2.0

The δ due to oxime CH₃ carbon in dimethylglyoxime exhibited at 9 ppm. This signal was shifted downfield between 9.30-9.61 ppm on coordination. Moreover, the δ for imine carbon exhibited at 154 ppm in free ligand of D. On the complexes this signal was shifted up field by 0.9-0.55 ppm¹⁻³.

The ¹³C NMR spectra of *N*-acetyl glycine show signals at 179.5, 176.70, 45.81 and 24.45 ppm due to the C1, C3, C2 and C4 respectively. The signal of C1 and C2 were shifted downfield by 0.5-2.2 and 0.19-1.09 ppm respectively. All these signals have indicated that the dimethylglyoxime and *N*-acetyl glycine were coordinated with the metal ions through the N and O atoms^{18,20}. All the data of ¹³C NMR for the ligands and their complexes were listed in Table 4.

Table 4. ¹³C NMR data (δ, ppm) of the free ligands and their complexes in DMSO-*d*₆

Compound	C=N-OH _D	CH ₃ _D	C1 _G	C3 _G	C2 _G	C4 _G
D	154	9	-	-	-	-
G	-	-	179.5	176.70	45.81	24.45
[Ni(D)(G)]	153.37	9.55	180	176	46.01	24.60
[Zn(D)(G)]	153.45	9.61	181.7	176.1	46	24.53
[Pd(D)(G)]	153.31	9.52	181.5	176.5	46.5	24.53
[Cd(D)(G)]	153.10	9.38	180.4	176.5	46.5	24.60
[Pb(D)(G)]	153.31	9.30	180	176.70	46.9	24.61

Magnetic susceptibility measurements

The magnetic moment for the prepared complex of VO(IV) ion was found to be 1.46 B.M within the expected value for one electron. The diamagnetic for the Ni(II) and Pd(II) complexes may be due to the low spin square planer. The complexes of Zn(II), Cd(II) and Pb(II) are also diamagnetic as expected from their electron configuration²¹. All the data and remarks are found in Table 5.

Table 5. The electronic spectra data and magnetic moments for the compounds

Compound	λ_{\max} n.m	Wave number cm^{-1}	ϵ_{\max} $\text{Lmol}^{-1}\text{cm}^{-1}$	Assignment	μ_{eff} B.M
D	266	37593	167	$\pi \rightarrow \pi^*$	-
	285	35087	351	$n \rightarrow \pi^*$	
G	251	39840	161	$\pi \rightarrow \pi^*$	-
	347	28818	188	$n \rightarrow \pi^*$	
[VO(D)(G)]	267	37453	1027	Charge transfer (C.T)	1.46
	289	34602	298	C.T	
	555	18018	20	${}^2B_2 \rightarrow {}^2B_1$	
	916	10917	18	${}^2B_2 \rightarrow {}^2E$	
	982	10183	12		
[Ni(D)(G)]	271	36900	2970	C.T	Diamagnetic
	362	27624	1390	C.T	
	372	26881	1402	C.T	
	445	22471	997	${}^1A_{1g} \rightarrow {}^1A_{2g}$	
	571	17513	1250	${}^1A_{1g} \rightarrow {}^1B_{1g}$	
[Zn(D)(G)]	267	37453	983	C.T (M→L)	Diamagnetic
	288	34722	279	C.T (M→L)	
[Pd(D)(G)]	268	37313	1340	C.T (M→L)	Diamagnetic
	293	34129	262	Red shift	
	514	19455	12	${}^1A_{1g} \rightarrow {}^1A_{2g}$	
	915	10928	14	${}^1A_{1g} \rightarrow {}^1B_{1g}$	
	980	10204	25		
[Cd(D)(G)]	267	37453	1141	C.T (M→L)	Diamagnetic
	289	34602	192	C.T (M→L)	
[Pb(D)(G)]	262	38167	232	C.T (M→L) blue shift	Diamagnetic
	267	37453	1225	C.T (M→L)	
	289	34602	175	C.T (M→L) red shift	

Electronic spectral studies

The electronic spectra of the dimethylglyoxime shows the absorption bands at 266 and 285 nm which are attributed to $\pi \rightarrow \pi^*$ and $n \rightarrow \pi^*$ transitions respectively. Thus, the electronic spectra of the *N*-acetyl glycine exhibited electronic transitions of $\pi \rightarrow \pi^*$ and $n \rightarrow \pi^*$ at 251 and 347 nm respectively.

The electronic spectra of the VO(IV) complex reveals bands at 555 and 916, 982 nm which are attributed to the electronic transition of ${}^2B_2 \rightarrow {}^2B_1$ and ${}^2B_2 \rightarrow {}^2E$ respectively. All these transitions corresponds to VO(IV) complex as a square pyramid²². The electronic spectra of the Ni(II) and Pd(II) complexes with an electronic configuration of d^8 shows new

absorption bands in the visible region at 445 and 514 nm respectively which these bands are attributed to the electronic transition ${}^1A_1g \rightarrow {}^1A_2g$ and the bands at 571 and 915, 980 nm respectively are caused by the electronic transition of ${}^1A_1g \rightarrow {}^1B_1g$. These assignments refers that the Ni(II) and Pd(II) complexes are square planer²².

Finally, the electronic configuration of Zn(II), Cd(II) and Pb(II) complexes was d^{10} which confirms the absence of any d-d electronic transitions. Nevertheless, the absorption bands in their spectra were suffered from red and blue shift with hyper chromic effects^{23,24}. All the absorption bands were fully assigned in Table 5.

Conclusion

A new mixed-ligand complexes of the general formula $[M(D)(G)]$ where D = dimethyl glyoximato monoanion, G = N-acetylglycinato and M = VO(IV), Ni(II), Zn(II), Pd(II), Cd(II) and Pb(II) were prepared and based on the presented results, the following conclusion can be drawn:

1. All the complexes are insoluble in water and most of organic solvents but soluble in DMF and DMSO- d_6 , as well as all of them are non-electrolyte.
2. The structure for the complexes based on UV-Vis, IR, (1H , ${}^{13}C$) NMR spectroscopy was proposed which is indicated that the dimethylglyoxime and N-acetylglycine were coordinated with the metal ions through the N and O atoms.
3. It can be suggested that the geometries of the prepared complexes are as follows:
 - a. Square pyramid geometry for the VO(II) complex (Figure 1).
 - b. Square planer geometry for the Ni(II) and Pd(II) complexes (Figure 2).
 - c. Tetrahedral geometry for the Zn(II) and Cd(II) complexes.
 - d. Irregular tetrahedral for the Pb(II) complex.

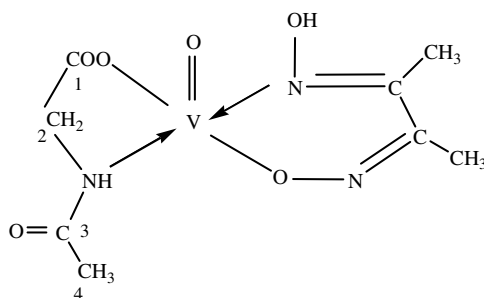


Figure 1. Square pyramid geometry for the $[VO(D)(G)]$ complex

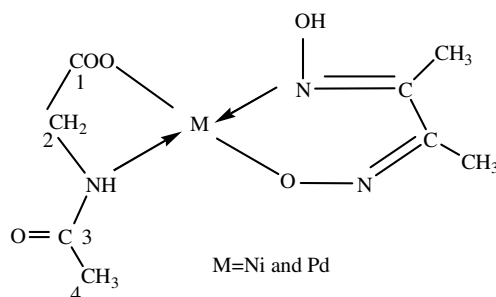


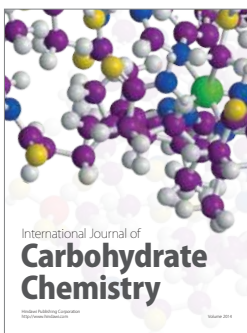
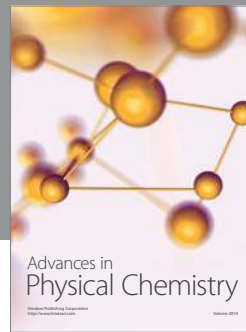
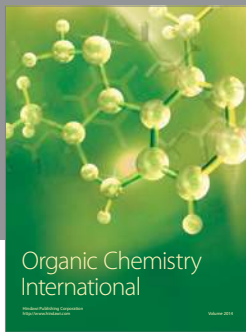
Figure 2. Square planer geometry for the $[M(D)(G)]$ complex

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