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Synthesis and Investigations of Some New Homobimetallic Complexes Involving Schiff Base Derived From Diketone and Amine

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Abstract

A bidentate Schiff base ligand; 2,3-Bis[N-(2,4-dinitrophenylhydrazineimino)butane(L), and its new homobimetallic complexes have been synthesized and characterized on the basis of analytical, spectral, magnetic and conductance measurements. The compositions of these complexes are found to be $[(M)_2L(\mu\text{-}CH_3COO)_2(\eta\text{-}CH_3COO)_2].XH_2O$ (where M=Co(II) or Cu(II), $[(Zn)_2L(\mu\text{-}CH_3COO)_2(\eta\text{-}CH_3COO)_2]$; and $[(Ni)_2L\ (\mu\text{-}CH_3COO)_2(\eta\text{-}CH_3COO)_2(H_2O)_4]\ XH_2O$. The overall IR data suggest the bidentate (NN) nature of the ligand and the metal centres are bridged by bidentate CH_3COO groups. The Co(II), Cu(II) and Zn(II) complexes are proposed to be square planar, while the Ni(II) complex is proposed to be octahedral.

الخلاصة

تضمن البحث تحضير وتشخيص ليكاند قاعدة شيف ثنائي السن، 3,2 بس[ن-(2، 4-ثنائي نايتروفنيل هيدرازين أيمينو) بيوتان(L)، وكذلك معقداته ثنائية النوى الجديدة. شخصت المعقدات بالطرق الفيزيائية، الكيميائية والطيفية المعروفة. ان الصيغ الكيميائية لهذه المعقدات هي:

$[(M)_2L(\mu\text{-}CH_3COO)_2(\eta\text{-}CH_3COO)_2].XH_2O$ (عندما M= كوبلت(II) أو نحاس(II))

$[(Zn)_2L(\mu\text{-}CH_3COO)_2(\eta\text{-}CH_3COO)_2]$و$XH_2O$ $[(Ni)_2L(\mu\text{-}CH_3COO)_2(\eta\text{-}CH_3COO)_2(H_2O)_4]$.

اظهرت قياسات الاشعة تحت الحمراء بان الليكاند ثنائي السن (NN) وكذلك وجود مجموعتي كاربوكسي ثنائية السن جسرية. يعتقد ان معقدات الكوبلت، النحاس والخارصين لها شكل مربع مستوي الاكثر احتمالاً، بينما معقد النيكل شكل ثماني السطوح الاكثر احتمالاً.

Introduction

Generally, Schiff base complexes have remained an important and popular area of research due to their simple synthesis, versatility and diverse range of applications(1-4). Bidentate Schiff bases with a NN donor atom set are well known to coordinate with various metal ions, rendering them of tremendous attraction(5,6). The ligand bonding through nitrogen to the central metal ions forms an important class of biologically active ligands(7,8). The studies on homobimetallic complexes in which the two metal centres are held in closed proximity have addressed ligand environment, redox behaviour, magnetic exchange interactions and spectroscopic properties, therefore these kind of complexes still continue to play a very important role in our understanding of various aspects of coordination chemistry of metals(9,10).Polynuclear complexes containing bridging groups are of current interest due to their versatile molecular topologies and wide applications(11-13). The carboxylate group is one of the most widely used bridging ligands for designing polynuclear metal complexes with interesting magnetic properties. Normally, each of the two oxygen atoms of a carboxylate group are bonded to a different metal ion to form a M–O–C–O–M bridge(14). The occurrence of M–O–M bridges via one oxygen atom of the carboxylate ligand is relatively scarce. Finally, binuclear complexes have been found to be better catalysts than the mononuclear complexes(15).

Keeping the importance of homobimetallic bridging Schiff bases complexes, the present article has been taken into account.

Experimental

Materials:

All chemicals used in this work were either Analar or Reagent grade used without purification such as

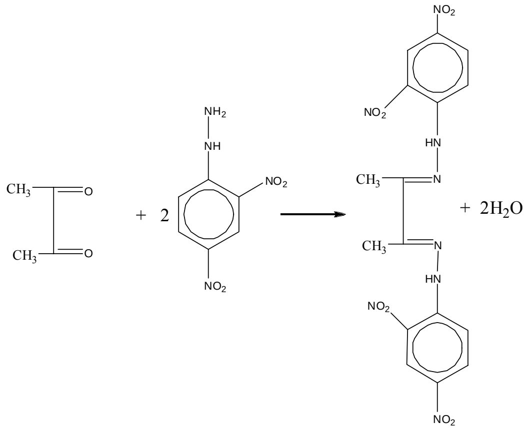
$Co(CH_3COO)_2.4H_2O$ (98%), $Ni(CH_3COO)_2.4H_2O$ (98%), $Cu(CH_3COO)_2.H_2O$ (98%), $Zn(CH_3COO)_2.2H_2O$ (98%), biacetyl (99%) and 2,4-dinitrophenylhydrazine (70%).

Analysis and physical measurements:

The metal contents were determined according to the standard procedure(16). Melting points were determined by using Electrothermal 9300 digital apparatus. Molar conductivities of the complexes have been measured in an electrolytic conductivity measuring set LF-42 using 0.001M dimethylformamide (DMF) solutions at room temperature. IR spectra were recorded on a Bruker (tensor 27) spectrophotometer in the 4000-400cm^{-1} range using KBr disc. Electronic spectra were recorded on a Shimadzu 1601 spectrophotometer in DMF at 25°C for 0.001M solution of the compounds using a 1cm quartz cell. Magnetic susceptibility measurements of the complexes in the solid state were determined by the Faraday method at room temperature using a Bruker B.M.6 apparatus.

Synthesis of the Schiff base (L):

An ethanolic solution of biacetyl (0.01mol.) was added to an ethanolic solution of 2.4-dinitrophenylhydrazine (0.02mol.) and refluxed for ~ 6 hours. The resulting solution was concentrated and the precipitate was separated by filtration, washed with ethanol and then air-dried.



(L)

Synthesis of the complexes:

A general method has been used for the synthesis of the homobimetallic complexes as follows:

A hot ethanolic solution of the ligand (0.01mol.) was added to the hot ethanolic solution of metal acetate hydrate (0.02mol.). The mixture was refluxed for 7 hours. The complexes thus formed were collected and washed with distilled water and ethanol to remove the unreacted starting materials and then were dried in air.

Results and discussion

All the prepared complexes were stable in air at temperature room. Their analytical data together with some physical properties are summarized in table 1. The reaction of metal acetate hydrate with the Schiff base (L) (molar ratio 2:1) yields complexes of the general formula $[(M)_2L(\mu\text{-}CH_3COO)_2(\eta\text{-}CH_3COO)_2].XH_2O$ as in the following equation:

$$2M\,(CH_3COO)_2.nH_2O + L \xrightarrow{\text{ethanol}} [(M_2)(\mu\text{-}CH_3COO)_2(\eta\text{-}CH_3COO)_2].XH_2O + yH_2O$$

M	n	x	y
Co(II)	4	(1 to 8)	(8 – x)
Cu(II)	1	(1 to 2)	(2 – x)
Zn(II)	2	0	0

While the reaction of $Ni(CH_3COO)_2.4H_2O$ with the Schiff base (L) (molar ratio 2:1) yields complexes of the general formula $[(Ni)_2L(\mu\text{-}CH_3COO)_2(\eta\text{-}CH_3COO)_2(H_2O)_4].XH_2O$
as in the following equation:

$$2Ni\ (CH_3COO)_2.nH_2O + L \xrightarrow{ethanol}$$
$$[(Ni)_2(\mu\text{-}CH_3COO)_2(\eta\text{-}CH_3COO)_2\ (H_2O)_4].\ XH_2O + yH_2O$$

M	n	x	y
Ni(II)	4	(1 to 4)	(4 – x)

Based on the metal content measurements have been supported the above general formulas , which shows that in each complex the ratio of metal: ligand is 2:1. The molar conductance of the complexes (Λ_M) in DMF is in the range (25-18)ohm^{-1} cm^2 mol^{-1} (Table 1), indicating a non-electrolytic in nature and that no inorganic anions such as CH_3COO^- ions are present in outer sphere coordination(17). The non-conducting character reveals the presence of (CH_3COO) groups and metal ions in the coordination sphere.

Table (1): Some physical and analytical properties of the compounds

Compound	Colour	m.p. C°	Yield %	% metal		Λ_M
				Calculated	Found	
L	Orange	312-314	74	-	-	-
$[(Co)_2L(\mu\text{-}CH_3COO)_2(\eta\text{-}CH_3COO)_2].XH_2O$	Brown	338-341 d*	29	(12.48-14.4)	13.88	25
$[(Ni)_2L(\mu\text{-}CH_3COO)_2(\eta CH_3COO)_2(H_2O)_4]XH_2O$	Oxide yellow	349-353 d	31	(12.44-13.2)	12.77	21
$[(Cu)_2L(\mu\text{-}CH_3COO)_2(\eta\text{-}CH_3COO)_2].XH_2O$	Dark cream	355-359 d	48	(15.03-15.36)	14.37	18
$[(Zn)_2L(\mu\text{-}CH_3COO)_2(\eta\text{-}CH_3COO)_2]$	Caramel	362-368 d	58	16.08	17.03	Very poor soluble

* d = decomposition

IR spectra:

The active site of the free ligand and its bonding to the metal atoms was characterized to comparison of the main infrared absorption bands of the free ligand and its complexes (Table 2). The main characteristic bands located in the ligand spectrum at 3103, 1644 and 1333cm^{-1}, which due to the ν(NH), ν(C=N) and ν(NO_2) stretching vibrations $^{(18-20)}$, respectively. Upon complexation, the broad bands observed in the range (3444-3420)cm^{-1}(except for the zinc complex) are attributable to the νH_2O frequencies of the coordinated or lattice water molecule$^{(21, 22)}$. The νC=N band at 1644 cm^{-1} is shifted to lower frequencies in all the complexes (1618-1613)cm^{-1}, which may be attributed to the coordination of the nitrogen atom of the azomethine group to the metal atoms$^{(23)}$, and forming five membered chelate ring. In the IR spectra of the complexes, the absoption bands in the regions (1592-1538) and (1422-1375)cm^{-1}, which are associated with the asymmetric and the symmetric stretching modes in carboxylates, respectively. The Δ*v* value (*v*as- *v*s) of the carboxylate is (170-155) cm^{-1}, provides a good evidence that the carboxylate group acts as bidentate bridging units to metal (II) ions$^{(24-26)}$. If the carboxylate groups are monodentate, one would expect a higher frequency for the antisymmetric C=O stretching in the range of 1650 to 1750cm^{-1}. The IR spectra of all the acetate complexes show an absorption band in the region (1698-1653)cm^{-1}that is assigned to the ν(COO^-)$_{as}$ asymmetric stretching vibrations of the acetate ion and another in the region (1280-1222)cm^{-1} that can be assigned to the *v*(COO^-)s symmetric stretching vibration of the acetate ion.

The difference between (v_{as}-v_s) of around (462-419) cm^{-1}, which indicates the monodentate coordination of the acetate group with the central metal ion$^{(27)}$. Finally, assignment of the proposed coordination sites is further supported by the appearance of new bands in the regions (616-497) and (511-427) cm^{-1}, which could be attributed to the formation of M–O and M–N bonds, respectively.

Table (2): important IR spectral bands (cm^{-1})

Compound	ν (H_2O)	ν (NH)	ν (C=N)	ν as $(COO)_{bri}$	ν s $(COO)_{bri}$	$\Delta\nu$	ν (NO_2)	ν as (COO) mono	ν s (COO) mono	$\Delta\nu$	M-O	M-N
L	-	3103	1644	-	-	-	1333	-	-	-	-	-
$[(Co)_2L(\mu\text{-}CH_3COO)_2(\eta\text{-}CH_3COO)_2].XH_2O$	3420	3105	1613	1538	1375	163	1349	1653	1234	419	510	427
$[(Ni)_2L(\mu\text{-}CH_3COO)_2(\eta\text{-}CH_3COO)_2(H_2O)_4].XH_2O$	3441	3104	1617	1590	1422	168	1338	1698	1280	418	497	470
$[(Cu)_2L(\mu\text{-}CH_3COO)_2(\eta\text{-}H_3COO)_2].XH_2O$	3444	3108	1616	1575	1420	155	1347	1683	1258	425	616	510
$[(Zn)_2L(\mu\text{-}CH_3COO)_2(\eta\text{-}CH_3COO)_2]$	-	3107	1618	1592	1422	170	1335	1684	1222	462	576	511

bri. = bridging
mono = monodantate

Electronic spectra and magnetic moments:

The electronic absorption spectra of the Schiff base and its complexes are recorded at room temperature using DMF as the solvent (Table 3). The electronic spectrum of the free ligand (L) shows two bands at 34246 and 21645 cm^{-1}, which are assigned to benzene $\pi \rightarrow \pi^*$ transition and the intraligand charge transfer band (INCT), respectively. Although the square planar complexes of Co(II) are not very common, the electronic spectrum of Co(II) complex exhibits two bands at 18135 and 19762cm^{-1} in DMF solution. This is attributable to $^2A_{1g} \rightarrow ^2B_{1g}$ and $^2A_{1g} \rightarrow ^2E_g$ transitions, respectively, in square planar geometry. The magnetic moment of Co(II) complex was found to be 2.24 B.M. This may be to the mixing of the higher ligand field term $^2A_{2g}$with $^2A_{1g}$ground term on account of spin-orbit coupling whereby the magnetic moment of the cobalt(II) complex goes above the spin value of 1.73 B.M(28-30). The electronic spectrum of the Ni(II) complex is consistent with the formation of an octahedral geometry with the appearance of three bands at 9803, 20408 and 21367cm^{-1}. These bands refer to the $^3A_{2g}$ (F) $\rightarrow ^3T_{2g}$(F) (ν_1), $^3A_{2g}$ (F) $\rightarrow ^3T_{1g}$ (F) (ν_2) and $^3A_{2g}$ (F) $\rightarrow ^3T_{1g}$ (P) (ν_3)(31), respectively. The octahedral geometry of Ni(II) ion in the complex is confirmed by the measured magnetic moment value, 2.89 B.M(32). The Cu(II) complex shows two d–d absorption bands at 18450 and 19685cm^{-1}corresponding to the $^2B_{1g} \rightarrow ^2A_{1g}$ and $^2B_{1g} \rightarrow ^2E_g$ transitions(31), respectively, supporting square planar configuration. The magnetic moment of the copper(II) complex has been found to be 1.67 B.M. This corresponds to the presence of one unpaired electron in the complex(32). The electronic spectral study of the complex $[(Zn)_2L(\mu\text{-}CH_3COO)_2(\eta\text{-}CH_3COO)_2]$ is unsuccessful due to its poor solubility in common organic solvents such as DMF and actually it shows a band at 28089 cm^{-1}may be assigned to the metal to ligand charge transfer. Finally, the absorption spectrum of Zn(II) complex shows on bands` due to d–d transition. This phenomenon is natural as there is no possibility of transition due to non-availability of empty d-orbital. This complex is found to be diamagnetic as expected for d^{10}configuration.

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Table (3): The electronic spectra and magnetic moments of the compounds

Compound	Band (nm)	Absorption region (cm^{-1})	Possible assignments	μ_{eff} (B.M)
L	292	34246	$\pi\rightarrow\pi^*$	-
	462	21645	INCT	
$[(Co)_2L(\mu\text{-}CH_3COO)_2(\eta\text{-}CH_3COO)_2].XH_2O$	472	21186	INCT	2.24
	506	19762	$^2A_{1g}\rightarrow{}^2E_g$	
	546	18315	$^2A_{1g}\rightarrow{}^2B_{1g}$	
$[(Ni)_2L(\mu\text{-}CH_3COO)_2(\eta\text{-}CH_3COO)_2(H_2O)_4].XH_2O$	468	21367	$^3A_{2g}(F)\rightarrow{}^3T_{1g}(P)$	2.89
	490	20408	$^3A_{2g}(F)\rightarrow{}^3T_{1g}(F)$	
	1020	9803	$^3A_{2g}(F)\rightarrow{}^3T_{2g}(F)$	
$[(Cu)_2L(\mu\text{-}CH_3COO)_2(\eta\text{-}CH_3COO)_2].XH_2O$	492	20325	INCT	1.67
	508	19685	$^2B_{1g}\rightarrow{}^2E_g$	
	542	18450	$^2B_{1g}\rightarrow{}^2A_{1g}$	
$[(Zn)_2L(\mu\text{-}CH_3COO)_2(\eta\text{-}CH_3COO)_2]$	356	28089	Charge transfer	Diamagnetic

INCT = Intraligand charge transfer

Conclusion

From the above discussion, and from the data given in Tables 1, 2 and 3, it is concluded that the Schiff base (L) in all the complexes coordinated as bidentate chelating ligand. Additional coordination of the carboxyl group was observed for the metal complexes, in which the metal centre is bridged by CH_3COO moieties. Further coordination at the nickel (II) ion was occurred with two molecules of water on the Z axes (axil ligand) to each nickel (figures 1, 2 and 3)

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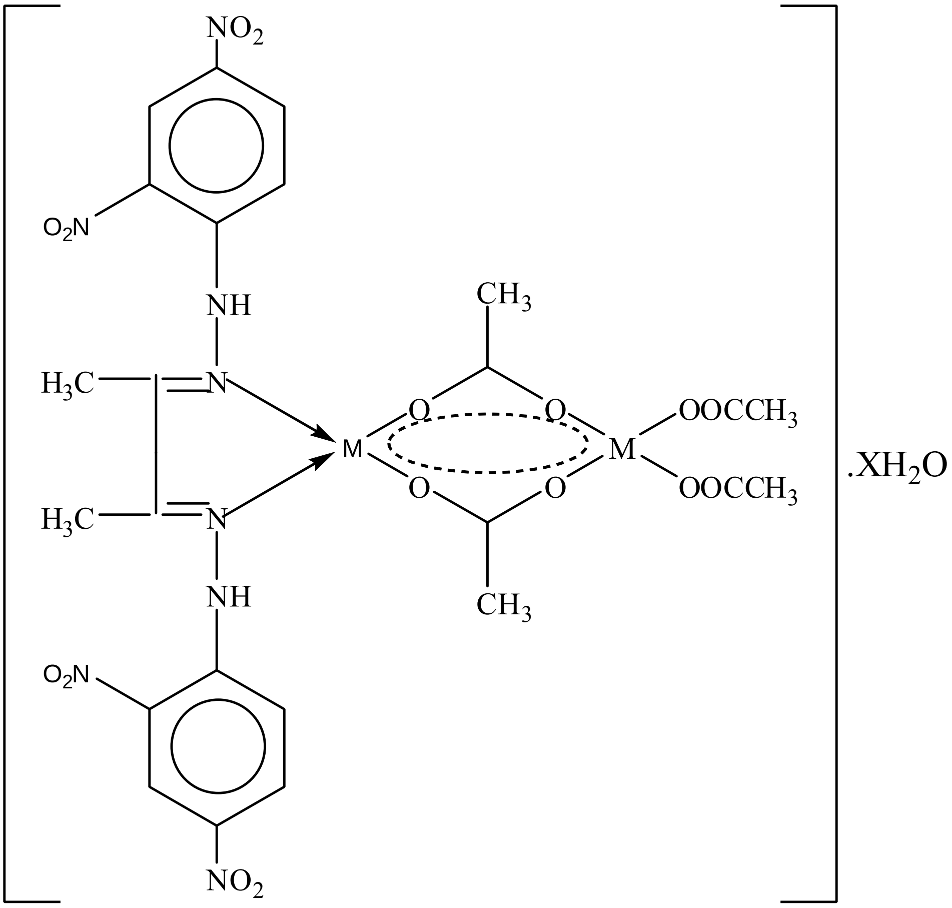
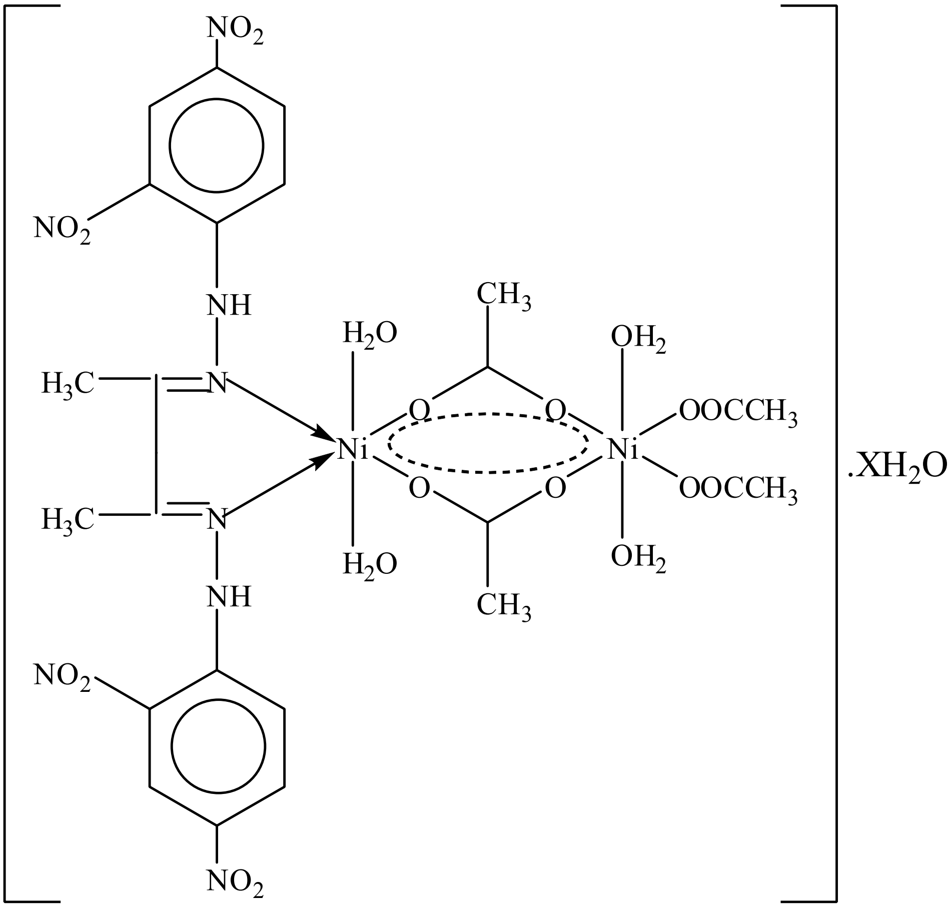


M = Co(II) or Cu(II)

Figure (1): Suggested structure of the square planar homobimetallic of 2,3-Bis[N-(2,4-dinitrophenylhydrazineimino)]butane-bis (μ -acetato)bis (η-acetato) dimetal (II, II). hydrate complexes



(X = 1 to 4)

Figure (2): Suggested structure of the octahedral homobimetallic of 2,3-Bis[N-(2,4-dinitrophenylhydrazineimino)]butane-bis (μ -acetato)bis (η-acetato) tetraaquadinickel (II, II). hydrate complex

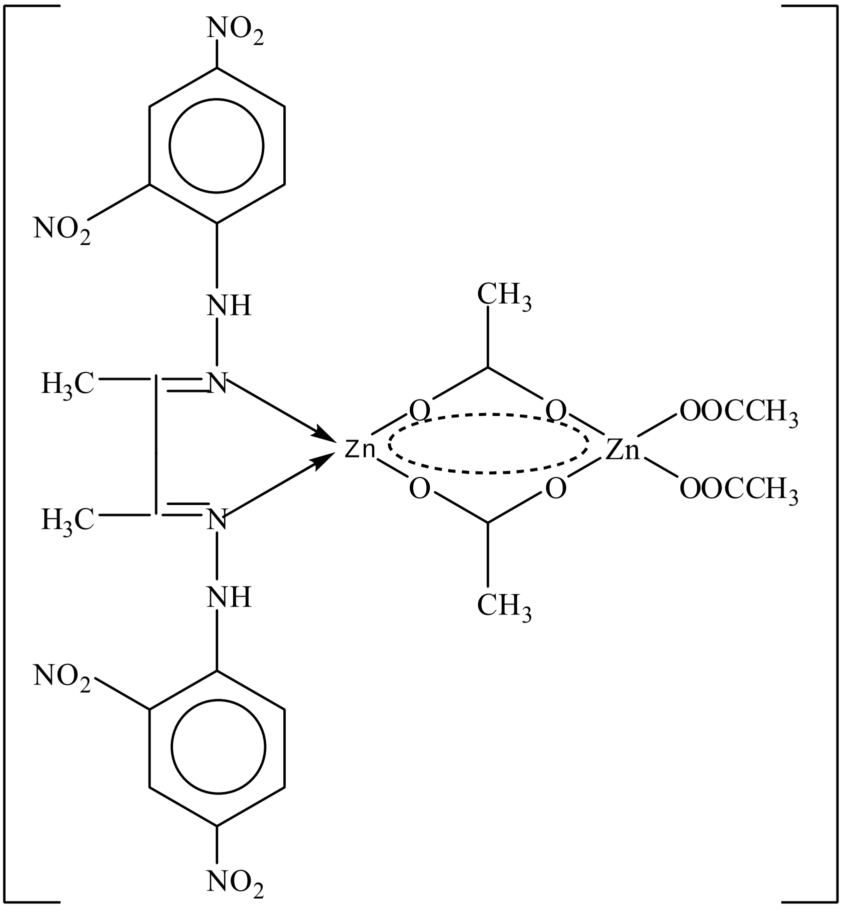


Figure (3): Suggested structure of the square planar homobimetallic of 2,3-Bis[N-(2,4-dinitrophenylhydrazineimino)]butane-bis (μ-acetato)bis(η-acetato)dizinc(II, II). complex

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