TRINUCLEAR VANILLIN-HYDRAZIDE SCHIFF BASE COMPLEXES OF COBALT, NICKELAND COPPER SALTS

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Abstract

In this work the preparation and characterisation of some new homo hetero tri-nuclear complexes of cobalt, nickel and copper . These complexes were prepared by the reactions of the chloride and nitrate salts of the above mentioned metals with the Schiff base ligand vanillidenesuccinohydrazide (VSH₄), derived by the condensation of vanillin and succinoloylhydrazine .

The isolated complexes have the general formulae : $[M_3(VSH_4)_2X_6]$, $[M_2M'(VSH_4)_2X_6]$, $[MM'M''(VSH_4)_2X_6]$, $K_2[M_3(VS)_2]$, $K_2[M_2 M'(VS)_2]$ and $K_2[MM'M''(VS)_2]$;where M, M' M'' are Co⁺², Ni⁺² and Cu⁺², respectively, VSH₄ and VS are the neutral and the tetra basic forms of the ligand and X = Cl or NO₃. Neutral complexes (Type I) obtained from neutral medium and anionic complexes (Type II) result from basic medium. The characterisation and studies of the ligand and its complexes were carried out by elemental microanalysis, molar conductance, magnetic susceptibility and spectral measurements .

The above different studies revealed that the metal ions are hexacoordinated in neutral complexes giving the most probable octahedral structure, while the anionic complexes are tetracoordinated with the expected tetrahedral or square planar geometries. In both types the ligand acts as hexadentate coordinating through carbonyl (or enol) oxygen, azomethine nitrogen and phenoxide oxygen atoms. The composition and stability for some of the complexes were studied in solution using Job method which showed 1:1 metal to ligand ratio and similar stability constants.

Introduction

Schiff base metal complexes have a key role in the development of coordination chemistry, resulting in an enormous number of publications ranging from pure synthetic work to modern physicochemical and biochemically relevant studies ^[1]. Schiff base ligands represent one of the most widely utilized classes of ligands in metal coordination chemistry. Their complexes have shown many important catalytic applications, ranging from asymmetric epoxidation ^[2,3], Lewis acid assisted organic transformations ^[4], to various types of polymerization ^[5,6]. The attractive features of Schiff base ligands are their unique electronic and bulky properties.

Recently, research work dealing with various aspects involving different physicochemical properties and complexation behaviour of tetradentate Schiff bases has appeared in the literature , primarily focusing in the separation of actinides from lanthanides in nuclear reprocessing ^[7] and catalytic properties ^[8]. Schiff bases have been used in the formation of polymers and polynuclear complexes ^[9-11].

Some of these complexes have been investigated for the chemical design of a new generation of magnetic, optics, electrical conductivity, catalysis and biology, all of which are derived from the effectiveness of the C- or N- bonded cyanide ion as bridging ligand between two metal ions ^[12-17].

Further more, some of the homodinucear complexes which posse's donor atoms or group, e.g., phenoxy oxygen atoms and immine nitrogen atoms, play a key role in the modelling of metallobisites and in the search for appropriate systems for activating simple molecules owing to their special coordination ability with the transition metal ions ^[16-20] Herein, we report the synthesis and characterisation of some homo and

hetero trinuclear complexes formed by the reactions of cobalt (II), nickel (II) and copper (II) salts with the Schiff base ligand vanillidenesuccinoloylhydrazide (VSH_4) .

Experimental

Materials and Methods

All the chemicals consumed used in this study were obtained commercially and used as supplied unless otherwise stated. Succinoloylhydrazide was prepared according to a known procedure by the condensation of diethylsuccinate with hydrazine hydrate ^[11] and used without further purification . Preparation of vanillidenesuccinoloylhydrazide (VSH₄) :

The ligand, vanillidenesuccinoloylhydrazide, was prepared by the condensation of ethanolic solutions (40 ml) of succinoloylhydrazine (1.46g, 0.01mol) and vanillin (3.04g, 0.02mol) using 1:2 molar ratio. On reflux for about 6 h and after cooling, the resulting yellow crystalline precipitate was filtered off, washed with cold ethanol and dried. The elemental analysis of this product gave :

Found : C, 58.25; H, 5.66; N, 13.81%

C₂₀H₂₂N₄O₆ requires : C, 57.95; H, 5.31; N, 13.52%

Preparation of the complexes

Two general procedures were followed for the preparation of the complexes. In all cases 3:2 metal to ligand ratio was used. For the hetero nuclear complexes, the different metal salts were dissolved in the same solution and reacted at the same time with the ligand.

a- Type I : to a solution of the metal salt (0.003mol in 30ml ethanol) was added an ethanolic solution of the ligand (0.002 mol, 0.828g in 40ml ethanol). The reaction mixture was refluxed for about 3 h. On cooling the precipitated complexes were filtered off washed with cold ethanol and dried .

b- Type II : to the same above mixture of the metal salt and the ligand an ethanolic solution of 0.1 N KOH was added slowly and with continuous stirring. The addition of KOH was continued until complete precipitation, afterward, the reaction mixture was simmered on a water bath for few minutes and then allowed to stand. The separated complexes were filtered off, washed with cold ethanol and dried .

Analysis and physical measurements

Analysis of the ligand and its complexes for carbon, hydrogen and nitrogen was carried out on Perkin-Elmer 2400 analyzer at the School of Chemistry, University of Birmingham-UK. Cobalt, nickel and copper were measured gravimetrically using standard methods [21]. Molar conductivity measurements were performed on 10⁻³M solutions in dimethylformamide (DMF) using LF-42 digital conductivity meter at room temperature. Infrared spectra were recorded on IR-300 and Pye-Unicam SP-1100 infrared spectrophotometers on the range of 400-4000 cm⁻¹ using KBr discs, at the College of Science, University of Salahaldean- Erbil. Shimadzu UV-160 A spectrophotometer was used for the electronic spectral measurements. The measurements were carried out on 10⁻³ M solutions of the complexes in dimethylformamide at room temperature using 1 cm quartz cell .

The magnetic susceptibility measurements were made by the Faraday method at room temperature using a Bruker BM6 instruments, at the College of Science, University of Mosul. Diamagnetic corrections were calculated using Pascal's constants^[22].

Results And Discussion

Two types, neutral (Type I) and anionic (Type II), of new trinuclear complexes by two stages reaction of the metal salt and the ligand according to the following equations:

 $3MX_2.nH_2O + 2VSH4 \longrightarrow [M_3(VSH_4)_2X_6] + 3nH_2O....(1)$

 $3MX_2.nH_2O + 2VSH_4 + 8KOH \rightarrow K_2[M_3(VS)_2] + 6KX + (8 + 3n)H_2O.....(2)$

Where M = Co, Ni, Cu or mixed two or three different metals. VSH₄ and VS are the neutral and tetrabasic forms of the ligand, respectively. X = Cl or NO₃ and n = 2, 3 or 6.

The different physicochemical studies confirmed the 3:2 metal to ligand ratio for both type I and II complexes as depicted in equations 1 and 2. The results are in good agreement with the analytical data given in Table 1. The complexes are stable in air and have high melting points (273-340 °C) but they are insoluble in water, cold ethanol and methanol. Their slight solubility in dimethylformamide (DMF) enables us to measure the molar conductivity in this solvent. The low values of molar conductance refer to the non-electrolytic nature of type I complexes and confirmed their neutrality. On the other hand, the

higher values for type II complexes indicate their 2:1 electrolytic nature and confirmed their anionic origin ^[23]. The values of molar conductivity measurements are shown in Table 1. For some of type I complexes Job method was applied to study the stability, while for type II complexes the precipitate formed on addition of KOH prevent the continuation of the measurements. The stability constants are similar as they have the same environments and similar compositions.

The infrared spectrum of the ligand is in good agreement with the formation of the proposed Schiff base which showed the absence of the aldehyde group of vanillin and the appearance of the new azomethine band characteristic for the Schiff base -C=N bond.

The infrared spectra of the ligand and type I complexes confirmed that coordination had occurred through both carbonyl oxygen, azomethine nitrogen and phenoxyl oxygen atoms. In case of type II complexes the coordination occurred via both enolic oxygen, azomethine nitrogen and phenoxy oxygen atoms. These conclusions were drawn from the lowering of the bands due to C=O, C=N and OH bonds upon coordination in type I complexes. For type II complexes, the disappearance of C=O, NH and OH bands confirm the above suggestion of coordination. The disappearance of these bands is due to the deprotonation in basic medium $^{[9, 10, 24, 25]}$ according to the following tautomeric transformation:

O O O

I

L

-C-NH-N=C- -C=N-N=C-

From the data of the infrared spectra given in Table 2 it was concluded that NO_3 coordinated as monodentate since there are three bands in the regions that represent the monodentate action of nitrate group ^[26].

The band due to Cl ion could not be observed due to the limitation of our spectrophotometer. In addition, two new bands *not found in the spectrum) were observed in the spectra of both types of the complexes and located at about 420-430 and 460-480 cm⁻¹, these bands were attributed to the stretching frequencies of M - O and M - N bonds, respectively ^[26].

The electronic spectral data are given in Table 3 together with the suggested structures of the complexes. For type I, the hexa-coordinated cobalt and nickel complexes, three bands were observed and assigned to the three allowed transitions in the visible region ${}^{[27]}$, ${}^{4}T_{1g}(F) {}^{4}T_{2g}(F) (v_1)$, ${}^{4}T_{1g}(F) \longrightarrow {}^{4}A_{2g}(F) (v_2)$, ${}^{4}T_{1g}(F) {}^{4}T_{2g}(F) (v_1)$, ${}^{4}T_{1g}(P) (v_3)$ and ${}^{3}A_{2g}(F) \longrightarrow {}^{3}A_{2g}(F) , {}^{3}T_{2g}(F) (v_1)$, ${}^{4}T_{1g}(F) \longrightarrow {}^{3}T_{1g}(F) (v_2)$, and ${}^{3}A_{2g}(F) \longrightarrow {}^{3}T_{1g}(P) (v_3)$ for cobalt and nickel complexes, respectively. The positions of these bands are characteristic for octahedral symmetry around cobalt and nickel ions. For hexa-coordinated

copper complexes, the single broad asymmetric band

below 15000 cm⁻¹ arises from ${}^{2}B_{1g} \longrightarrow {}^{2}A_{1g}, {}^{2}B_{1g} \longrightarrow {}^{2}B_{2g}, {}^{2}B_{1g} \longrightarrow {}^{2}E_{g}$ transitions .

Since this band is broad, asymmetrical and below 15000cm⁻¹, therefore distorted (Jahn-Teller distortion) octahedral structure was suggested [28]. The degree of covalence in the coordination bonds of these complexes was inferred from β -values which is low for cobalt complexes indicating the high proportion of covalence and high for nickel complexes suggesting low covalent character ^[29,30] For the tetracoordinated type II complexes only one band (v₃) was observed in their electronic spectra which is due to ${}^{4}A_{2}(F) \longrightarrow {}^{4}T_{1}(P) (v_{3}) \text{ and } {}^{3}T_{1}(F) \longrightarrow {}^{3}T_{1}(P)$ (v₃) transitions in tetrahedral field. The other two bands (v_1) and (v_2) could not be observed due to our spectrophotometer limits. For the tetra-coordinated copper complexes, the position of the single band around 19000 cm⁻¹ suggested square planar geometry

In the electronic spectra of the mixed cobalt and nickel complexes several bands were observed in the visible region and assigned as due to octahedral and tetrahedral structures for both type I and type II complexes, respectively ^[27]. For those complexes containing three metals, the spectra involved many bands and are very complicated .

All the complexes showed charge-transfer bands of π - π^* transition which they represent an indication for the presence of some π - bonding character in the coordination bonds between the metal and the ligand active sites. This type of π bonding is most probably due to the partial donation of the electronic density to the ligand empty π^* - orbital from the metal filled π orbital.

In Table 1 the values of the magnetic moments are given . The values are in good agreement with the predicted high-spin octahedral and tetrahedral environments for cobalt (II) and nickel (II) .

ions having d⁷ and d⁸ systems, respectively, and agree well with the presence of 3 and 2 unpaired electrons

in each system . The lowering of the values for spinonly magnetic moments is most probably related to the presence of some antiferromagnetism as a result of the supper exchange mechanism between the adjacent metallic centres in the complexes. For copper (II) complexes, orbital contribution or some sort of supper exchange mechanism by the involvement of the ligand results in a little higher values than the expected spin-only moment of one unpaired electron, d⁹-system [31]. The stability constants and the nature of the complexes were studied in neutral solution (Type I) only, while for type II such study can not be conducted due to the precipitation upon KOH addition . It was notice that only 1:1 metal-ligand species are possible (in contrast to the 3:2 ratios in the solid state) and all have nearly similar stabilities (The values of the stability constant for the studied complexes were found ranging between $1.32 \times 10^4 - 1.79 \times 10^4$). Such results could be explained as due to the similar environments for the complexes .

Conclusion

From the above physicochemical and spectral studies it was concluded that the ligand acted as neutral hexadentate in type I giving neutral complexes where the coordination occurred through both carbonyl oxygen. azomethine nitrogen and phenoxyl oxygen atoms and the inorganic ligands, chloride and nitrate ions coordinated as monodentate resulting in hexacoordinated metal ions with octahedral geometry. For type II, as a result of deprotonation in basic medium, coordination occurred through enolic oxygen , azomethine nitrogen and phenoxy oxygen atoms. In these tetra-coordinated species, tetrahedral structure was suggested for cobalt and nickel complexes and square planar geometry for copper complexes. In the solid state, trinuclear complexes were obtained (Figures I and II) while in solution only 1:1 species were possible due to the weakness of HO-M bonds that could not maintain the trinuclear framework .

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Compound	cm ohm mol in DMF	Colour	MP C°	µeff (BM)	A analysis %, Found (Calculated)					
					С	Н	N	М	Cl	
	36	Dark yellow	278	3.79	35.06	3.38	14.45	12.76		
[C03(VSH4)2(NO3)6]					(34.86)	(3.19)	(14.53)	(12.83)		
[C03(VSH4)2 Cl6]	32	Green	279	4.02				14.43	17.42	
								(14.41)	(17.47)	
[Ni ₃ (VSH ₄) ₂ (NO ₃) ₆]	34	Pale yellow	270					12.86		
								(12.80)		
[Ni ₃ (VSH ₄) ₂ Cl ₆]	36	Yellowish-green	273	2.80				14.38	17.49	
		1 A A A A A A A A A A A A A A A A A A A						(14.47)	(17.48)	
[Cu ₃ (VSH ₄) ₂ (NO ₃) ₆]	39	Dark olive	290		34.00	3.40	14.34	13.73		
					(34.51)	(3.16)	(14.09)	(13.71)		
[Cu ₃ (VSH ₄) ₂ Cl ₆]	40	Brown	290	2.28				15.27	17.30	
								(15.48)	(17.27)	
[CoNiCu(VSH ₄) ₂ (NO ₃) ₆]	38	Yellow	291	3.02				Co,4.18(4.26)		
								Ni,4.30(4.25)		
1								Cu,4.65(4.60)		
K ₂ [Co ₃ (VS) ₂]	132	Brown	308					16.53		
								(16.44)		
K ₂ [Ni ₃ (VS) ₂]	131	Pale brown	315	2.20	44.43 (44.68)	3.08	!0.14	16.41		
99989 275929 8 0 75527						(3.35)	10.42)	(16.39)		
$K_2[Cu_3(VS)_2]$	140	Pale green	320	2.19				17.52		
								(17.50)		
K ₂ [Co ₂ Ni(VS) ₂]	152	Yellowish green	314	3.26				Co,10.49(10.38)		
								Ni,5.58(5.51)		
K ₂ [Ni ₂ Co(VS) ₂]	160	Yellow	299	3.16				Ni,10.89(10.93)		
								Co,5.51(5.48)		
$K_2[Co_2Cu(VS)_2]$	130	Pale green	328	3.59				Co,10.89(10.91)		
								Cu,5.76(5.88)		
K2[Cu2Ni(VS)2]	158	Green	340	2.81				Cu,11.75(11.72)		
								Ni,5.62(5.55)		
K ₂ [Cu ₂ Co(VS) ₂]	142	Pale green	318		44.48	3.37	10.50	Cu.11.68(11.72)		
		8			(44.27)	(3.32)	(10.33)	Co,5.39(5.48)		
K ₂ [Ni ₂ Cu(VS) ₂]	146	Pale green	336	2.64				Ni,10.86(10.88)		
								Cu,5.91(5.88)		
K ₂ [CoNiCu(VS) ₂]	143	Brown	302	4.12				Co,5.97(5.36)		
		1						Ni,5.43(5.35)		
a contract of the second se								Cu,5.90((5.88)		

Table (1) Analytical data and some physical properties

Table (2) Some important infrared spectral data (cm⁻¹)

Type I-Complexes	V _(OH)	V _(NH)	V(C	(=0)	V _(C=N)	δ _(OH)	V(N-N)	V(M-	V(M-	v(NO ₃)	
								N)	0)		
VSH ₄	3490	3240	16	90	1605	1290	1005				
[Co ₃ (VSH ₄) ₂ (NO ₃) ₆]	3445	3240	16	60	1560	1250	1030	465	420	955,1385,1515	
[Co ₃ (VSH ₄) ₂ Cl ₆]	3400	3250	16	60	1585	1270	1030	470	420		
[Ni ₃ (VSH ₄) ₂ (NO ₃) ₆]	3400	3240	16	50	1590	1270	1030	470	420	980,1385,1515	
[Ni ₃ (VSH ₄) ₂ Cl ₆]	3400	3205	16	40	1580	1270	1033	465	430		
[Cu ₃ (VSH ₄) ₂ (NO ₃) ₆]	3410	3240	16	60	1580	1265	1025	460	430	970,1385,1510	
[Cu ₃ (VSH ₄) ₂ Cl ₆]	3410	3240	16	65	1590	1265	1025	465	420		
[CoNiCu(VSH ₄) ₂ (NO ₃) ₆]	3400	3205	16	35	1585	1260	1035	460	425	990,1385,1520	
Type II-Complexes	V(C-N)	v(azine)		v (C-	V _(N-N)		v _(M-N)		V _(M-O)	
$K_2[Co_3(VS)_2]$	1580	1600	- 0)		60	0 1025		460		410	
$K_2[Ni_3(VS)_2]$	1560	1590		11	55	1025		455		410	

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$K_2[Cu_3(VS)_2]$	1580	1590	1160	1025	460	420
K ₂ [Co ₂ Ni(VS) ₂]	1570	1588	1160	1030	455	420
$K_2[Ni_2Co(VS)_2]$	1565	1590	1160	1025	460	420
$K_2[Co_2Cu(VS)_2]$	1565	1590	1160	1030	440	410
$K_2[Cu_2Ni(VS)_2]$	1560	1585	1160	1025	460	420
$K_2[Ni_2Cu(VS)_2]$	1565	1595	1160	1025	455	420
K ₂ [Cu ₂ Co(VS) ₂]	1565	1595	1160	1025	460	420
K ₂ [CoNiCu(VS) ₂]	1560	1590	1160	1025	460	425



Compound	v ₁	v ₂	V3	C.T	10D _q	β	v_2/v_1	CFSE	Structure
[Co ₃ (VSH ₄) ₂ (NO ₃) ₆]	10625	14365	22615	33115	11995	0.310	1.35	9593	Octahedral
[Co ₃ (VSH ₄) ₂ Cl ₆]	10930	14145	22830	31850	11900	0.254	1.29	9522	Octahedral
[Ni ₃ (VSH ₄) ₂ (NO ₃) ₆]	10265	16340	27030	3225	10265	0.775	1.58	12340	Octahedral
[Cu ₃ (VSH ₄) ₂ Cl ₆]	14600			31850	14600			8759	Octahedral
[Co ₂ Cu(VSH ₄) ₂ (NO ₃) ₆]	10640	14375	22225	34000	11570	0.280	1.35	9260	Octahedral for
	13230			31150	13230			7935	Co&Cu
[CoNiCu(VSH ₄) ₂ (NO ₃) ₆]	10385		22140	31440	12060				Octahedral
	10635	16430	26465	34385	10635	0.73	1.55	12450	for Co, Ni & Cu
	14300			30125	14300			8530	
K ₂ [Ni ₃ (VS) ₂]			14235	33115					Tetrahedral
			14325	32030					
K ₂ [CoNiCu(VS) ₂]			13605	35475					Co,Ni-Tet.
	19335			30425					Cu-Sq.



Fig.I- Type I-Complexes



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معقدات ثلاثية النواة لأملاح الكويلت والنيكل والنحاس مع قواعد شيف من نوع فانلين – هيدرازيد

عصام جرجيس سلومي ، وجدان عبد الغني الزيدان قسم الكيمياء ، كلية التربية ، جامعة الموصل ، الموصل ، العراق لا شالا تارير 2 / 12 / 2010 مستقد القدار 17 / 2 / 2012

(تاريخ الاستلام: 3 / 12 / 2012 ---- تاريخ القبول: 17 / 6 / 2013)

الملخص

يستعرض هذا البحث تحضير ودراسة عددا من المعقدات ثلاثية النواة متجانسة وغير المتجانسة للكوبلت والنيكل والنحاس مع ليكاند من نوع قاعدة شيف مشتق من تفاعل التكثيف للفائلين مع السكسينويل هيدرازين . لقد تم الحصول على المعقدات من تفاعل كلوريدات ونترات هذه الفلزات مع اليكاند المذكور في كل من الوسطين المتعادل والقاعدي. لهذه المعقدات الصيغ العامة : ,[M2M'(VSH4)2X_6], [M2M'(VSH4) [M3(VSH2)], K2[M2M'(VS)] و [MM'M'(VS)2] و [MM'M'(VS)2], K2[M2M'(VS)2], K2[M2M'(VS)2] اذ يمثل كل من :"M,M',M ايونات الكوبلت والنيكل والنحاس و VS, VSH4 الشكل المتعادل ورباعي القاعدة لليكاند و X ايون الكلور او النترات .

شخصت المعقدات التي تم الحصول عليها يطرق مختلفة، تحليلية وطيفية ومغناطيسية ، واتضح من هذه الدراسات ان اليكاند يعمل بشكل سداسي السن متعادل في الوسط المتعادل وسداسي السن رباعي القاعدة في الوسط القاعدي . وعليه فقد نتجت عن الوسط المتعادل معقدات متعادلة تأخذ فيها الفلزات التتاسق السداسي ذو بنية ثماني السطوح وعن الوسط القاعدي معقدات ايونية سالبة لها التتاسق الرباعي ذو بنية رباعي السطوح والمربع المستوي . اجرينا ايضا دراسة لطبيعة واستقرار بعض من هذه المعقدات في المحلول المتعادل باستخدام طريقة جوب واتضح ان للمعقدات النسب التكوينية 1:1 فلز – ليكاند في المحلول (على خلاف ما هو ملاحظ لمعقدات الحالة الصلبة ، 2:3 فلز -ليكاند) وظهرت ثوابت الأستقرار التي تم الحصول عليها في تشابه ملموس وذلك لكن العوامل المحيطة والمؤثرة على تكوين هذه المعقدات متساوية تقريبا .