

Metal Complexes as ligands: Trinuclear Alkali Metal Complexes with Nickel(II) and Copper(II) Metal Complexes of Violuric Acid (Isonitrosobarbituric Acid)

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Abstract: In the present study we have synthesized new trinuclear complexes of alkali metal salts with interaction of stable metal chelates of violuric Acid of Ni(II) & Cu(II) having general formula $[Ma(H_2Va)_2(M_bL)_2]$ and $[Ma(H_2Va)_2(M_bX)_2]$ where $M_a = Ni(II)$ or $Cu(II)$ and $M_b = Li^+, Na^+ & K^+$, $H_2Va =$ deprotonated Violuric Acid, $L =$ deprotonated 1-nitroso-2-naphthol or 8-hydroxyquinoline and, $X = ClO_4^-$ or SCN^- . The IR spectral studies suggests that the Ni(II) & Cu(II) metal chelates act as ligand and coordination towards alkali metal salts takes place through free ketonic oxygen atom as well as the oxygen atom of the oximino group. The diffuse reflectance electronic spectra and magnetic moment values of the metal chelates and trinuclear complexes with alkali metal salts indicates the change in geometry during oxygen bridged complex formation.

Keywords: Violuric Acid (isonitrosobarbutric Acid), 1-nitroso-2-naphthol, 8-hydroxyquinoline, Metal complexes as ligands

1. Introduction

Violuric acid, the 5-oximino derivatives of barbutric acid, is known to exist as a mixture of keto-enol tautomers.¹ Mortan and Tippling² cited its pK value as 4.7 Welcher³ mentioned the possibility of violuric acid as an analytical reagent for chromatographic separation of cations. Much work has been reported with alkali metal salts of Violuric acid⁴⁻⁶ from the point of view of color and chemical constitutions. Kuster⁷ discussed the reaction of ferrous ion with violuric acid.

Peter et. al.⁸, reported the formation of violurate complexes of Cu(II) that occur in ratio 2:1 in spectrophotometric determination of copper with violuric acid. Complexation reaction of Co(II) with Violuric acid in solution has also been studied spectrophotometrically⁹ and used for the selective determination¹⁰⁻¹³ of metals. Singh et al.¹⁴ reported the synthesis and characterization of Co(III) complexes of violuric acid.

The metal ligand constant with Violuric Acid was investigated by B.P. Singh et al.¹⁵. The Crystal structure of Cu(II) complex is reported by K. Tamaki et. al.¹⁶. The thermal behavior of yttrium (III)- violurate complexes was reported by A.A.N Gad et. al.¹⁷. The antiviral & Antibacterial properties of Co(III) complex with violuric acid was investigated by Eddie L et al.¹⁸ N.M. Korotchnoko¹⁹ reported the stability of violurate complexes of some d- & f metals and showed that violuric acid behaves as either mono or dibasic depending on the conditions. Isonitrosobarbutric acid i.e. violuric acid (H_3Va) which act in their deprotonated form (H_2Va^-) as bidentate Ligand via the oximino nitrogen atom N⁷ and the carbonyl-oxygen atom O⁸ as shown by X-ray study²⁰.

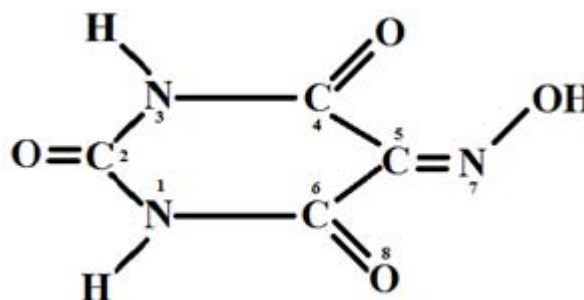


Figure 1:

The aim of this work is to prepare new complexes by the interaction of Ni(II) & Cu(II) metal chelates of violuric acid as “Metal complexes as ligand” towards alkali metals salts, which may be useful in understanding the transport and absorption mechanism of alkali metals ions from soil to plants.

2. Experimental

Materials

Ni (II) & Cu(II) acetate were used of E. Merck quality. The organic acid were used; 8-hydroxyquinoline and 1-nitroso-2-naphthol of BDH A.R. Quality, Violuric acid (H_3Va) was prepared by the method as described^{21,22}

Preparation of Ni (II) & Cu (II) metal chelates of Violuric Acid

Ni(II) and Cu (II) chelates of violuric acid were prepared according to known method^{9,13}.

Preparation of alkali metal salts of organic acids.

95 % ethanolic solution of 0.01 mole of organic acid and 0.01 mole of alkali metal hydroxide were mixed. The mixture was refluxed on magnetic hot plate for 1 hours with continuous stirring at 80⁰ C & on cooling the resulting solution, a

characteristic color precipitate was obtained. It was filtered washed with pure solvent and dried in an electric oven at 100° C.

Preparation of trinuclear complexes of Ni(II) and Cu(II) metal chelates with alkali metal salts.

Our usual method of synthesis was to take metal chelates Ni(H₂Va)₂ or Cu(H₂Va)₂ in an absolute ethanol and to add alkali metal salts to it in 1:2 mole ratio, usually slight excess of alkali metal salts were taken. The reaction mixture was refluxed with constant stirring in hot magnetic plate for about 3 to 4 hours at 60° C. The whole substance went in to the solution and subsequently the adduct were precipitated in hot condition during the process of refluxing. They were filtered, washed several times with absolute ethanol and dried in oven at 80° C.

3. Results and Discussion

The adducts are stable under dry condition, but decompose on exposure to moisture, as such they were kept in a desiccators over anhydrous CaCl₂. Some physical properties and analytical data of the metal chelates and their adducts are listed in Table-1. From the results, It is evident that the adducts have characteristic color and are different from the metal chelates. All the adducts show high melting/decomposition temperatures which indicate their greater stability.

Infrared spectra

All the infrared spectral measurements were made in KBr disk for ligand and complexes between 4000-200cm⁻¹ and 4000-650cm⁻¹. Characteristic IR bands (cm⁻¹) of the metal complexes as well as their alkali metal adducts are shown in Table-2. The IR spectra of H₃Va²³, Na[H₂Va], K[H₂Va]·2H₂O, Rb[H₂Va]²⁴ [Ru(II)(H₂Va)₃]²⁵ and [NH₄][Fe(II)(H₂Va)₃]²⁶. have been reported.

Table 1

Compound	Color	Transition (t ⁰ C) or decomposition (d ⁰ C) temperature	Magnetic moment values in B.M.	%Analysis found/calc.				
				C	H	N	M _a	M _b
Ni(H ₂ Va) ₂	Bluish White	>320,175t	2.78	25.02 (25.89)	1.31 (1.07)	22.26 (22.65)	15.24 (15.83)	
Ni(H ₂ Va) ₂ . (NaIN2N) ₂	Brown	315d	----	43.49 (44.16)	2.32 (2.10)	14.52 (14.72)	7.48 (7.71)	5.98 (6.04)
Ni(H ₂ Va) ₂ .(KIN2N) ₂	Brown	300d	3.28	41.79 (42.38)	2.27 (2.01)	13.84 (14.12)	7.16 (7.40)	9.39 (9.83)
Ni(H ₂ Va) ₂ . (Li8HQ) ₂	Light Pink	>300	----	45.78 (46.38)	2.50 (2.37)	16.23 (16.64)	8.42 (8.72)	
Ni(H ₂ Va) ₂ . (Na8HQ) ₂	Yellow	>320	----	43.73 (44.27)	2.57 (2.27)	15.56 (15.89)	8.01 (8.33)	6.08 (6.52)
Ni(H ₂ Va) ₂ .(K8HQ) ₂	Greenish White	>320	3.38	41.86 (42.34)	2.39 (2.17)	15.02 (15.20)	7.39 (7.96)	10.21 (10.58)
Ni(H ₂ Va) ₂ .(NaClO ₄) ₂	Yellowish Cream	>320,180t	3.31	15.51 (15.59)	0.98 (0.64)	13.23 (13.64)	9.21 (9.53)	7.03 (7.47)
Ni(H ₂ Va) ₂ .(KSCN) ₂	Dull White	212d	3.38	20.88 (21.25)	0.86 (0.70)	19.62 (19.83)	9.89 (10.39)	13.51 (13.81)
Cu (H ₂ Va) ₂	Yellowish Brown	240d	1.16	24.92 (25.56)	1.19 (1.06)	21.97 (22.36)	16.36 (16.91)	
Cu (H ₂ Va) ₂ .(NaIN2N) ₂	Brown	>320	----	42.96 (43.89)	2.17 (2.09)	14.38 (14.63)	7.83 (8.30)	5.69 (6.00)
Cu (H ₂ Va) ₂ . (KIN2N) ₂	Brown	>320	1.84	41.82 (42.12)	2.16 (2.00)	13.69 (14.04)	7.72 (7.96)	9.48 (9.78)
Cu (H ₂ Va) ₂ .(Li8HQ) ₂	Pink	>320	----	45.23 (46.04)	2.51 (2.36)	16.27 (16.53)	9.16 (9.37)	
Cu (H ₂ Va) ₂ .(Na8HQ) ₂	Pink	>320	1.88	43.06 (43.97)	2.39 (2.25)	15.59 (15.78)	8.61 (8.95)	6.38 (6.48)
Cu (H ₂ Va) ₂ .(K8HQ) ₂	Sky Blue	290d	----	41.59 (42.06)	2.28 (2.15)	14.81 (15.10)	8.36 (8.56)	10.17 (10.52)
Cu (H ₂ Va) ₂ .(NaClO ₄) ₂	Brown	260d	----	14.91 (15.47)	0.81 (0.64)	13.21 (13.53)	9.97 (10.23)	7.26 (7.41)
Cu (H ₂ Va) ₂ .(KSCN) ₂	Green	215d	2.21	20.86 (21.06)	0.83 (0.70)	18.98 (19.66)	10.79 (11.15)	13.43 (13.69)

4. Color, Decomposition temperature, magnetic moments & Elemental analysis of the complexes

The most characteristic vibrations e.g.v (C²=O), v(C⁴=O), v(C⁶=O⁸), v(C⁵=N⁷) and v(N⁷=O⁹) of the metal chelates of

violuric acid have also been assigned by reference to date on analogue complexes²⁷⁻³³. In Ni(II)and Cu(II) metal chelates of Violuric acid vC²=O, vC⁴=O, vC⁶=O⁸ and vN-O have been assigned at 1720, 1680, 1530, 1250cm⁻¹ and 1730,1680,1525 and 1235 cm⁻¹ respectively. In the trinuclear alkali metal adducts of Ni(H₂Va)₂, the vC⁴=O stretching frequency shifts to 1690-1700cm⁻¹ and the vN-O

stretching frequency shows higher shift to 1270-1285cm⁻¹ suggesting the involvement of oxygen atom of ketonic group (C⁴=O) and oxygen atom of oximino group in coordination with alkali metal ion in the trans structure of metal chelates .

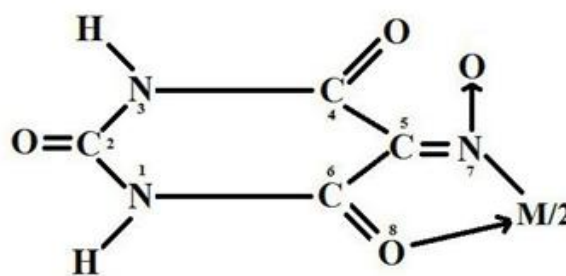


Figure 2:

Table 2: Pertinent IR data (cm⁻¹) for metal chelates as well as their adducts with alkali metal salts.

Adducts	ClO ₄ / SCN ⁻	Free ν C ² =O	ν C ⁴ =O	ν C ⁶ =O ⁸	ν N-O	ν M-N	ν M-O
Ni(H ₂ Va) ₂		1720m	1680w	1530sh	1250vs	580vs	500vs,430s
Ni(H ₂ Va) ₂ (Na8HQ) ₂		1720br	1702br	1540h	1285s	585s	500vs,440s
Ni(H ₂ Va) ₂ (K8HQ) ₂		1712s	1695sh	1540sh	1270vs	585s	505vs,440s
Ni(H ₂ Va) ₂ (NaIN2N) ₂		1715s	1690br	1520s	1280s	585s	500vs,435br
Ni(H ₂ Va) ₂ (KIN2N) ₂		1720s	1690s	1520s	1285s		
Ni(H ₂ Va) ₂ (NaClO ₄) ₂	1135vs, 1110m, 1000w	1720sh	1700w	1535w	1275s	590s,570s	500vs,440s
Ni(H ₂ Va) ₂ (KSCN) ₂	2075	1715s	1690s	1535br	1280vs	585vs	500vs,440s
Cu(H ₂ Va) ₂		1730s	1680s	1525br	1535vs	595vs	565vs,380s
Cu(H ₂ Va) ₂ (Na8HQ) ₂		1718sh	1700sh	1525sh	1580br	585vs	500vs,535br
Cu(H ₂ Va) ₂ (K8HQ) ₂		1720sh	1690sh	1530sh	1280br	580vs	500vs,400w
Cu(H ₂ Va) ₂ . NaIN2N) ₂		1720sh	1700sh	1520br	1300br		
Cu(H ₂ Va) ₂ . (KSCN) ₂	2070	1720sh	1700br	1520sh	1285br	580vs, 445m	500ws,410s

S=strong, m=medium, w=weak, sh=shoulder and br=broad

Similarly in the case of alkali metal adducts of Cu(H₂Va)₂, the νC⁴=O and νN-O stretching frequency shift to 1690-1700 and 1270-1300cm⁻¹ respectively, which indicate the coordination of alkali metal ion through oxygen atom of C⁴=O group as well as oxygen atom N-O group in the trans position of Cu(H₂Va)₂.

In the adducts of alkali metal thiocyanate, the thiocyanate peak shows at 2070-2075 cm⁻¹. The shifting of the νC=N to higher frequency (for KSCN and NaSCN 2020cm⁻¹) suggest coordination of alkali metal thiocyanate.

Similarly the adducts of alkali metal perchlorate the presence of band in the region at 1110-1135 cm⁻¹ and 1000cm⁻¹ suggest coordination of alkali metal perchlorate through the ketonic as well as oximino group atom.

In the lower region, the band at 580 and 565 cm⁻¹ might be attributed to a Ni-N vibration in Ni(II) and Cu(II) metal chelates respectively. The appearance of the band in the region 500-300cm⁻¹ are probably due to metal oxygen bond as well as bridging oxygen metal bond in adducts of metal chelates.

These evidences indicate that adduct formation is taking place through oxygen atom of oximino group as well as ketonic oxygen atom.

Magnetic Measurement

Magnetic susceptibility measurements were made using the faraday technique at 34° C. The results are recorded in Table-01

The magnetic moment value of Ni(H₂Va)₂ was found 2.78 B.M at room temperature. Halder et al.³⁴ reported the μ_{eff}

value 2.76 B.M at 293° K for the complex, bis (isonitrosoacetophenone) Ni(II), which are very close to the spin only value for two unpaired electron in octahedral Ni(II) metal ion. They also showed that the magnetic moment of the Ni(II) complex vary from 2.76 B.M at 293°K to 1.98 B.M at 80°K, indicating antiferromagnetic interaction. On the basis of the above observations the dimeric nature of the Ni(II) complex was proposed. A similar behavior was also reported by Lintvedt et al.³⁵

So on the basis of above facts the Ni(H₂Va)₂ complex has an octahedral stereochemistry. The magnetic moments values of isolated alkali metal adducts are found in between 3.28 to 3.54 B.M, which is higher than the magnetic moment values of alkali metal adducts of Ni(H₂Va)₂ may be due to change in the geometry of Ni(II) complexes of violuric acid in the adducts from octahedral structure to tetrahedral structure.

The magnetic moment of Cu(H₂Va)₂ is found 1.16 at room temperature. Which is markedly lower than the spin only value. Similar subnormal values was also observed by Natrajan et al.³⁶ and Halder et al.³⁷ for the bis(isonitrosoacetophenoate) Cu(II) and bis (isonitrososacetylacetonate) Cu(II) complexes respectively and suggested that this lower magnetic value is due to antiferromagnetic interaction and this may arises through molecular association involving oxobridges. The trinuclear alkali metal adducts of Cu(H₂Va)₂ display magnetic values between 1.84 to 2.21 B.M.³⁸

Thus it is evident that the trinuclear adducts are magnetically dilute and their magnetic moment values fall in the range of planar or tetrahedral Cu(II) complexes.³⁹⁻⁴⁰

Electronic spectra

All diffuse reflections electronic spectra were recorded on SHIMADZU UV-VIS-160A spectrometer in Nujol mull/Paraffin liquid. The diffuse reflectance spectra of Ni(H₂Va)₂ complexes in Nujol mull show the bands in region 240-360nm due to charge transfer, the bands at 575nm and 1020nm are assigned due to d-d transition.

Table 3: Major diffuse reflectance bands (nm) of metal chelates and their adducts

Compound	Diffuse reflectance (nm)
Ni(H ₂ Va) ₂	1020w,575br,360s,330s,240s
Ni(H ₂ Va) ₂ .(K8HQ) ₂	1050w,608br,410s,331s,240s
Ni(H ₂ Va) ₂ .(KIN2N) ₂	1040w,602br,400s,320s,242s
Ni(H ₂ Va) ₂ .(NaClO ₄) ₂	1100br,735br,475sh,375s,329s,240s
Ni(H ₂ Va) ₂ .(KSCN) ₂	1060w,609br,500sh,366s,340s,235s
Cu(H ₂ Va) ₂	650w,450w,343s,301s,237s
Cu(H ₂ Va) ₂ .(K8HQ) ₂	1080w,700sh,613br,416br,334s,239s
Cu(H ₂ Va) ₂ .(KIN2N) ₂	1100w,710sh,425br,330s,239s
Cu(H ₂ Va) ₂ .(KSCN) ₂	1035w,617br,449br,326w,299w,247s
Cu(H ₂ Va) ₂ .(NaClO ₄) ₂	1010w,700sh,475br,341s,301s,258br

Br=broad, s=strong,m=Medium,w=weak, sh=shoulder and h=hump

The absorption bands of alkali metal adducts of Ni(H₂Va)₂ is found in the region 608-735 nm and a band of low intensity observed around 1030 to 1100 nm suggests the change in stereochemistry of Ni(H₂Va)₂ from octahedral to tetrahedral structure and the magnetic moment values observed higher than 3.25B.M. further confirm the tetrahedral structure if Ni(II) the alkali metal adducts.

In the Cu (H₂Va)₂ complex charge transfer bands appears in the region 237 to 343nm. The weak band at 450nm and a weak shoulder at 650nm are attributed to d-d transition band. In the alkali metal adducts of Cu(II) violurate, the d-d transition bands show the change in intensity and position. Which clearly indicate the change in the stereochemistry⁴¹ of Cu violurate as well as the adduct formation with alkali metal salts.

5. Structure & Bonding

On the basis of elemental analysis, the molecular formula of trinuclear alkali metal adducts has been suggested as [M_a(H₂Va)₂.(M_bL)₂] or [M_a(H₂Va)₂.(M_bX)₂] where M_a=Ni (II) or Cu (II) and M_b=Li⁺, Na⁺ or K⁺, L=deprotonated 1-nitroso-2-naphthol and 8-hydroxyquinoline, X= ClO₄⁻, SCN⁻ or Cl⁻.

The infrared spectral studies of these adducts, suggest that, complex ligand, i.e. Ni(II) and Cu(II) chelates of violuric acid acts as a Lewis base to the Lewis acid (alkali metal salts); Coordination is taking through the free ketonic oxygen atoms as well as the oxygen atom of the oximino group. The probable structure of the complexes may be produced schematically as such.

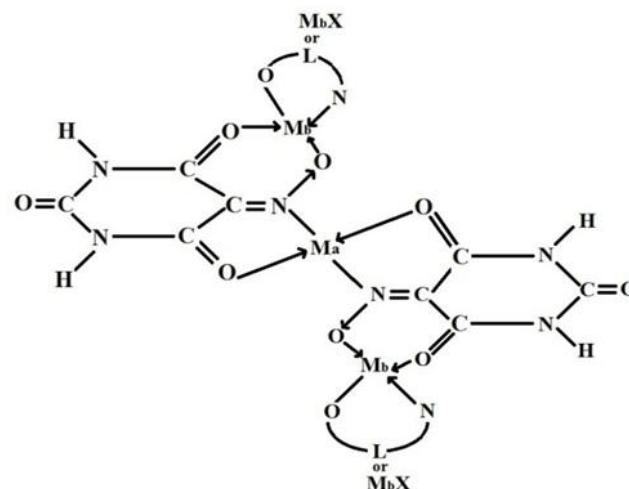


Figure 3

6. Acknowledgement

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