

## Synthesis and Characterization of Some Complexes of Cr(II) with 3-Cyano-2(1H)-pyridone Derivatives as Ligands

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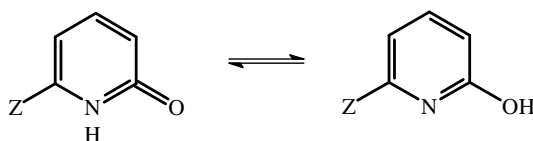
By reaction of acetates of Cr(II) [ $\text{Cr}_2(\text{O}_2\text{CCH}_3)_4 \cdot 2\text{H}_2\text{O}$ ] with the sodium salt of 3-cyano-2(1H)-pyridone derivatives, the dimeric compounds of  $\text{Cr}_2(\text{L})_4 \cdot \text{H}_2\text{O}$ , (L = 3-cyano-6-methyl-; 3-cyano-4,6-dimethyl-; 3-cyano-5,6-dimethyl-; 3-cyano-6-isopropyl-; 3-cyano-6-phenyl-2(1H)-pyridone) have been synthesized. These complexes have been characterized by elemental analysis, FTIR,  $^1\text{H}$ NMR, UV-Vis spectra and atomic absorption spectrometer and have been ascertained that the nitrogen atom of the cyano group remain without coordinated. In all complexes, anion 3-cyano-2(1H)-pyridone derivatives act as 1,3-bridging ligands. The stability of all five complexes is remarkably high. These complexes appear to be stable toward dry air at 25°C indefinitely, but exposure to moisture-saturated air causes a slight greenish ting to appear after *ca.* 10 d.

**Key Words:** 3-Cyano-2(1H)-pyridones,  $\text{Cr}^{2+}$  Complexes, Quadruple bonds.

### INTRODUCTION

The bridging ligands that are stereoelectronically similar to the carboxylate ions have played a major role in the growth of the field of quadruple bonded M–M compounds. Examination of the literature shows an abundance of experimental bridging ligands studies. The anion of 2-pyridone and its substituted derivatives have found their use in coordination chemistry as 1,3-bridging ligands and they behave similarly to carboxylates<sup>1</sup>. The first reported pyridone complexes of the chromium triad were the dimers of formula  $[\text{M}_2(\text{mhp})_4]$  (M = Cr, Mo, W and mhp = -methyl-2-pyridone), synthesized by Cotton *et al.*<sup>2</sup>.

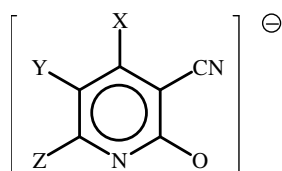
The tautomerism between neutral 2-pyridinols and 2-pyridone is one of the simplest examples of heterocyclic tautomerism and has been known since 1907. It has been extensively studied and was authoritatively reviewed by Karitzky and others<sup>3</sup>.



The presence of two tautomeric forms, which can be influenced by substituents, is potentially important in the coordination chemistry of these ligands. In the solution, polar solvents strongly favour the pyridone form, while in non-polar solvents both tautomers can exist. In the solid state, the pyridone form is often favoured.

Among the ligands that have been found to be suitable for the formation of quadruple bonded compounds of the type  $\text{Cr}_2\text{L}_4$ , the heterocyclic anions of 3-cyano-2(1H)-pyridone derivatives, as (L), have not been used.

Different derivatives of 3-cyano-2(1H)-pyridone, that the structure of its anions are as follow have prepared and their complexes are studied.



	1	2	3	4	5
X	H	CH <sub>3</sub>	H	H	H
Y	H	H	CH <sub>3</sub>	H	H
Z	CH <sub>3</sub>	CH <sub>3</sub>	CH <sub>3</sub>	iPr	pH

In this work, some complexes of Cr(II) with 3-cyano-2(1H)-pyridone derivatives were synthesized and spectral properties of complexes are studied.

### EXPERIMENTAL

All the compounds were treated as air sensitive and were handled on a nitrogen atmosphere using standard schlenk techniques. Liquid were transferred *via* polyethylene catheters through suba-seal fittings. All the experimental were carried out at room temperature.

$\text{Cr}_2(\text{O}_2\text{CCH}_3)_4 \cdot 2\text{H}_2\text{O}$  were prepared according to established procedures<sup>4</sup>. The 3-cyano-6-methyl-2(1H)-pyridone was purchased from Aldrich Chemical Co. The other ligands were prepared by the standard literature procedure<sup>5</sup>. All compounds and solvents were from Merck Chemical Co. All solvents and Schlenk tubes were deoxygenated prior to use by Biocen Dse 412 w vacuum pump and 99.99 % dinitrogen. The solvents were all dried distilled by standard procedures prior to use.

The infrared spectra were recorded as a KBr plate on a Mattson 1000 FTIR spectrometer. <sup>1</sup>H NMR spectra were recorded with a Bruker, 400 MHz, Ultrashield in DMSO-*d*<sub>6</sub> with TMS as internal reference. UV-Vis

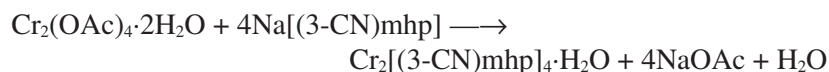
spectra were recorded with UV/Vis Philips in DMF. Elemental analysis of complexes were carried out by using Perkin Elmer C, H, N, analyzer model 240 B. Chromium concentration was analyzed using a Philips PU 9100X atomic absorption spectrometer.

### Synthesis of complexes

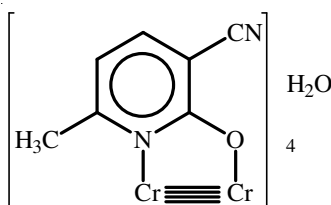
For synthesis of complexes, a typical reaction that is presented by Cotton *et al.*<sup>2</sup> is used. In this reaction, NaOCH<sub>3</sub> was dissolved in absolute ethanol before added H(3-CN)mhp ligand. After complete dissolution of ligand, chromium acetate was added with vigorous stirring. But Cr(II) is converted to the green Cr(III) and complexes of Cr(II) are not formed. This reaction is repeated for the other ligands and in all reactions, the results were the same that their reason is not turned out.

To obtain Cr(II) complexes, methanol was used instead of ethanol and sodium metal and 3-cyano-2(1H)-pyridone derivatives were added to this solvent. After all the sodium had reacted, chromium acetate was added and the slurry was stirred for a few hours at room temperature. After which a yellow, crystalline product was precipitated. The compound was filtered, washed with 2-propanol and dried under vacuum at room temperature. This method was used for all complexes. The stability of all 5 complexes is remarkably high. These complexes appear to be stable toward dry air at 25°C indefinitely, but exposure to moisture-saturated air causes a slight greenish ting to appear after about 10 d.

### Synthesis of Cr<sub>2</sub>[(3-CN)mhp]<sub>4</sub>·H<sub>2</sub>O (complex 1)



To prepare the first complex we added 0.08 g of sodium metal and 0.45 g of 3-cyano-6-methyl-2(1H)-pyridone, [(3-CN)mhp], to the 15 mL of methanol. After all the sodium had reacted, 0.31 g of Cr<sub>2</sub>(O<sub>2</sub>CCH<sub>3</sub>)<sub>4</sub>·2H<sub>2</sub>O was added and the slurry was stirred for 6 h at room temperature. The yellow crystalline product was precipitated. The compound was filtered, washed with 20 mL of 2-propanol and dried under vacuum at room temperature for 3 h. The yield of product was 65.7 %. Table-1 shows different analysis results of this complex.

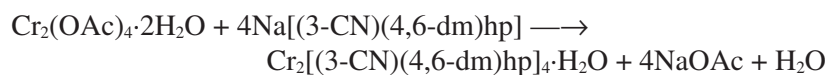


The following complexes (2, 3, 4, 5) were synthesized in a similar manner.

TABLE-1  
DIFFERENT ANALYSIS RESULTS OF  $\text{Cr}_2[(3\text{-CN)mhp}]_4\cdot\text{H}_2\text{O}$

FT-IR	3462, 3020, 2860, 2228, 1564, 1487, 1450, 1333, 1217, 930, 831, 631
$^1\text{H}$ NMR (DMSO- $d_6$ ):	$\delta$ 2.49 (s, $\text{H}_2\text{O}$ ), 2.50 (s, 3H, Me), 7.19(d, 1H, H-5), 8.996 (d, 1H, H-4)
Elemental analysis Found (Calcd.)	C = 51.24(51.37); H = 3.32(3.36); N = 17.08(17.12); Cr = 15.1 (15.9)
UV-Vis	$\alpha$ region = 415 nm, $\beta$ region = 369 nm, $\gamma$ region = higher energy

### Synthesis of $\text{Cr}_2[(3\text{-CN})(4,6\text{-dm})\text{hp}]_4\cdot\text{H}_2\text{O}$ (complex 2)



The yield of this complex (complex 2) was 64 % and the different analysis results are shown in Table-2.

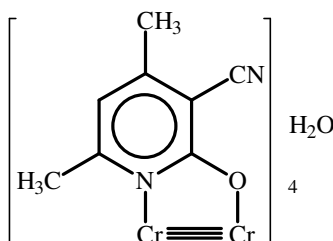
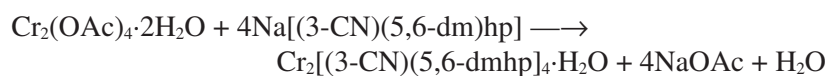


TABLE-2  
DIFFERENT ANALYSIS RESULTS OF  $\text{Cr}_2[(3\text{-CN})(4,6\text{-dm})\text{hp}]_4\cdot\text{H}_2\text{O}$

FT-IR	3467, 3031, 2907, 2220, 1532, 1550, 1490, 1330, 1225, 1148, 932, 839, 716, 639, 531, 469
$^1\text{H}$ NMR (DMSO- $d_6$ ):	$\delta$ 2.39 (s, $\text{H}_2\text{O}$ ), 2.66 (s, 3H, Me), 2.72(s, 3H, Me), 8.19 (s, 1H, H-5)
Elemental analysis Found (Calcd.)	C = 53.94(54.08); H = 4.18(4.22); N = 15.73(15.77); Cr = 14.32 (14.64)
UV-Vis	$\alpha$ region = 430 nm, $\beta$ region = 384 nm, $\gamma$ region = higher energy

### Synthesis of $\text{Cr}_2[(3\text{-CN})(5,6\text{-dm})\text{hp}]_4\cdot\text{H}_2\text{O}$ (complex 3)



The yield of this complex (complex **3**) was 65 % and the different analysis results are shown in Table-3.

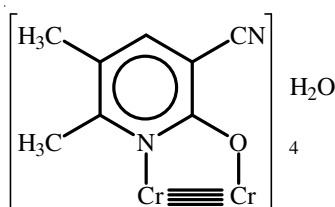
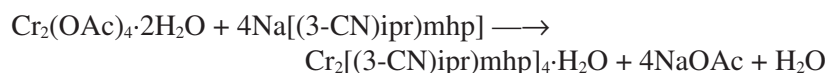


TABLE-3  
DIFFERENT ANALYSIS RESULTS OF  $\text{Cr}_2[(3\text{-CN})(5,6\text{-dm})\text{hp}]_4 \cdot \text{H}_2\text{O}$

FT-IR	3412, 3015, 3122, 2791, 2235, 1547, 1440, 1341, 1240, 1017, 947, 685
$^1\text{H}$ NMR (DMSO- $d_6$ ):	$\delta$ 2.12 (s, $\text{H}_2\text{O}$ ), 2.32 (s, 3H, Me), 2.57(s, 3H, Me), 8.62 (s, 1H, H-4)
Elemental analysis Found (Calcd.)	C = 53.83(54.08); H = 4.15(4.22); N = 15.63(15.77); Cr = 14.23 (14.64)
UV-Vis	$\alpha$ region = 425 nm, $\beta$ region = 379 nm, $\gamma$ region = higher energy

#### Synthesis of $\text{Cr}_2[(3\text{-CN})(\text{ipr})\text{hp}]_4 \cdot \text{H}_2\text{O}$ (complex **4**)



The yield of this complex (complex **4**) was 63 % and the different analysis results are shown in Table-4.

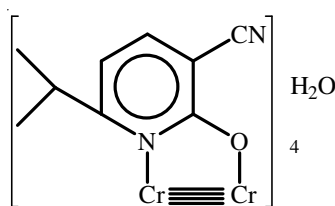
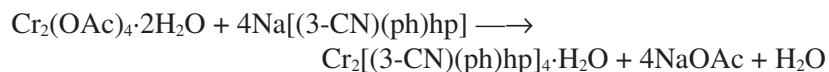


TABLE-4  
DIFFERENT ANALYSIS RESULTS OF  $\text{Cr}_2[(3\text{-CN})(\text{ipr})\text{hp}]_4 \cdot \text{H}_2\text{O}$

FT-IR	3465, 3146, 3030, 2993, 2228, 1565, 1472, 1375 (doublet), 1333, 1194, 993, 885, 816, 592
Elemental analysis Found (Calcd.)	C = 56.25(56.39); H = 4.90(4.96); N = 14.58(14.62); Cr = 12.98 (13.57)
UV-Vis	$\alpha$ region = 408 nm, $\beta$ region = 360 nm, $\gamma$ region = higher energy

**Synthesis of Cr<sub>2</sub>[(3-CN)(ph)hp]<sub>4</sub>·H<sub>2</sub>O (complex 5)**

The yield of this complex (complex 5) was 62 % and the different analysis results are shown in Table-5.

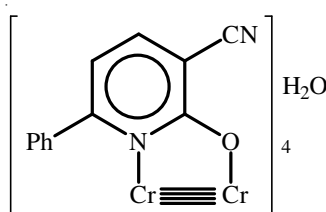


TABLE-5  
DIFFERENT ANALYSIS RESULTS OF Cr<sub>2</sub>[(3-CN)(ph)hp]<sub>4</sub>·H<sub>2</sub>O

FT-IR	3459, 3109, 3010, 2228, 1561, 1510, 1317, 1233, 1109, 901, 770, 693, 585, 523
Elemental analysis Found (Calcd.)	C = 63.70(63.86); H = 3.28(3.32); N = 12.38(12.41); Cr = 11.05 (11.53)
UV-Vis	α region = 402 nm, β region = 356 nm, γ region = higher energy

**RESULTS AND DISCUSSION**

FTIR spectra are used to determine whether coordination occurs through the cyano or the ring nitrogen in 3-cyano-2(1H)-pyridone derivatives complexes.

The complexes of protonated 2-pyridone ligands are bound through the exocyclic oxygen to the metals, ring nitrogen is not participate in coordination. In all these complexes, the proton attached to the ring nitrogen atom is involved in hydrogen bonding, which may be intramolecular or intermolecular. By means of controlling the direction of hydrogen bonding, Hamilton constructed an extended helical channel structure from a simple monomer subunit. This type of hydrogen-bonded self-assembly of three-dimensional copper(I) complexes of 3-cyano-6-methyl-2(1H)-pyridone having channels the size of which can be adapted to take in a variety of changing the hydrogen-bonding mode and distances<sup>7</sup>. In the deprotonated 2-pyridone ligands, the metals are bound to the ring nitrogen and the exocyclic oxygen.

Cyano group can be identified easily since they exhibit sharp  $\nu(\text{CN})$  at 2220-2000  $\text{cm}^{-1}$ . Upon coordination to a metal, the  $\nu(\text{CN})$  shift to higher

frequencies<sup>8</sup>. The CN<sup>-</sup> ion acts as  $\sigma$ -donor by donating electrons to the metal and also as a  $\pi$ -acceptor by accepting electrons from the metal.  $\sigma$ -Donation tends to raise the  $\nu(\text{CN})$  since electrons are removed from the 5  $\sigma$ -orbital, which is weakly antibonding, while  $\pi$ -back bonding tends to decrease the  $\nu(\text{CN})$  because the electrons enter into the antibonding  $2p\pi^*$  orbital. In general, CN<sup>-</sup> is a better  $\sigma$ -donor and a poorer  $\pi$ -acceptor than CO<sup>8</sup>. Thus the  $\nu(\text{CN})$  of the complexes are generally higher than the value for free CN<sup>-</sup>, whereas the opposite prevails for the CO complexes<sup>8</sup>. In 3-cyano-2(1H)-pyridone derivatives complexes,  $\nu(\text{CN})$  value is same in the appropriate complexes and ligands. Thus these complexes coordinate to chromium *via* the ring nitrogen, cyano nitrogen is not participated in coordination. Table-6 lists the important frequencies of these complexes and ligands.

TABLE-6  
LISTS OF THE IMPORTANT FREQUENCIES OF THE COMPLEXES  
AND LIGANDS

C/L	Vibrational mode							
	$\nu(\text{O-H})$	$\nu(\text{C-H})$ Arom.	$\nu(\text{C-H})$ Aliph.	$\nu(\text{N-H})$ Str.	$\nu(\text{CN})$	$\nu(\text{C=O})$	$\nu(\text{C=C})$	$\nu(\text{CN})$ Arom.
1/1'	3462/-	3020/-	2926, 2860/-	-/2930	2228/ 2228	1564/ 1672	1487/ 1564, 1487	1333/ 1325
2/2'	3467/-	3031/-	-/2907	-/2907	2220/ 2220	1532/ 1634	1550, 1490/ 1550, 1490	1330/ 1329
3/3'	3412/-	3015/-	3112, 2791/-	-/2791	2235/ 2235	1547/ 1665	1487/ 1572, 1487	1341/ 1341
4/4'	3465/-	3146, 3030/-	2993/-	-/3030, 3146	2228/ 2228	1565/ 1665	1472/ 1583, 1472	1333/ 1333
5/5'	3459/-	3109, 3010/-	-/-	-/2968	2228/ 2228	1561/ 1657	1510/ 1564, 1510	1317/ 1317

C/L = Complex/Ligand

The  $\nu(\text{NH})$  stretching are 3100-2900  $\text{cm}^{-1}$  regions and  $\nu(\text{NH})$  bending are 1640-1550  $\text{cm}^{-1}$  regions in right  $\nu(\text{CO})$  that often are covered by CO bands. These bands are omitted in FT-IR spectra of complexes that confirmed ring nitrogen is coordinated to chromium as N<sup>-</sup>.

The carbonyl group of 2-pyridines exhibits strong and sharp  $\nu(\text{CO})$  bands at 1670-1640  $\text{cm}^{-1}$ . Since  $\nu(\text{CO})$  is generally free from coupling with other modes and is not obscured by the presence of other vibration, studies of  $\nu(\text{CO})$  alone often provide valuable information about the structure and bonding of carbonyl complexes. In the majority of compounds,  $\nu(\text{CO})$  of ligands is shifted to lower frequencies. If CO forms a bridge between two metals; its  $\nu(\text{CO})$  is much lower than that of the terminal CO group<sup>8</sup>. The chromium oxidation state in compounds is VI ( $d^0$ ), V ( $d^1$ ), IV ( $d^2$ ), III ( $d^3$ ), II ( $d^4$ ) that in these synthesized complexes chromium is in oxidation state II ( $d^4$ ). The  $\nu(\text{CO})$  of  $\text{H}(3\text{-CN})\text{mhp}$  is 1672  $\text{cm}^{-1}$  that is shifted to 1564  $\text{cm}^{-1}$  in  $\text{Cr}_2[(3\text{-CN})\text{mhp}]_4\cdot\text{H}_2\text{O}$ . Thus CO group is coordinated to chromium through the oxygen in this complex. The  $\nu(\text{O-H})$  stretching of the coordinated water exhibit 3462  $\text{cm}^{-1}$  in this complex. For other complexes the case is the same: the  $\nu(\text{CO})$  of  $\text{H}(3\text{-CN})(4,6\text{-dm})\text{hp}$  is 1634  $\text{cm}^{-1}$  that is shifted to 1532  $\text{cm}^{-1}$  in  $\text{Cr}_2[(3\text{-CN})(4,6\text{-dm})\text{hp}]_4\cdot\text{H}_2\text{O}$ . The  $\nu(\text{O-H})$  stretching of the coordinated water exhibit 3467  $\text{cm}^{-1}$  in this complex.

The  $\nu(\text{CO})$  of  $\text{H}(3\text{-CN})(5,6\text{-dm})\text{hp}$  is 1665  $\text{cm}^{-1}$  that is shifted to 1547  $\text{cm}^{-1}$  in  $\text{Cr}_2[(3\text{-CN})(5,6\text{-dm})\text{hp}]_4\cdot\text{H}_2\text{O}$ . The  $\nu(\text{O-H})$  stretching exhibit 3412  $\text{cm}^{-1}$  in this complex.

The  $\nu(\text{CO})$  of  $\text{H}(3\text{-CN})(\text{iPr})\text{hp}$  is 1665  $\text{cm}^{-1}$  that is shifted to 1565  $\text{cm}^{-1}$  in  $\text{Cr}_2[(3\text{-CN})(4,6\text{-dm})\text{hp}]_4\cdot\text{H}_2\text{O}$ . The  $\nu(\text{O-H})$  stretching exhibit 3465  $\text{cm}^{-1}$  in this complex.

The  $\nu(\text{CO})$  of  $\text{H}(3\text{-CN})(\text{ph})\text{hp}$  is 1657  $\text{cm}^{-1}$  that is shifted to 1561  $\text{cm}^{-1}$  in  $\text{Cr}_2[(3\text{-CN})(\text{ph})\text{hp}]_4\cdot\text{H}_2\text{O}$ . The  $\nu(\text{O-H})$  stretching exhibit 3459  $\text{cm}^{-1}$  in this complex. In all of complexes the CO group is coordinated to chromium through the oxygen.

In general, metal-metal stretching,  $\nu(\text{M-M})$ , of these appear in the low-frequency region because the (M-M) bonds are relatively weak and the masses of metals are relatively large. If the complex is perfectly Centre symmetric with respect to the (M-M) bond at the center,  $\nu(\text{M-M})$  is forbidden in the infrared. If it is not,  $\nu(\text{M-M})$  may appear weakly in the infrared<sup>8</sup>. The  $\nu(\text{M-M})$  in the complex of  $\text{Cr}_2(\text{map})_4$ , 556  $\text{cm}^{-1}$  has been reported<sup>9</sup>. The bands in the high-frequency region are not metal sensitive since they originate in the hetero cyclic or aromatic ring of the ligand. Thus the main interest has been focused on the low-frequency region, where  $\nu(\text{M-N})$  and other metal sensitive vibrations appear. It has been difficult, however, to assign  $\nu(\text{M-N})$  empirically since several ligand vibrations also appear in the same frequency region.

The C-H aromatic stretching exhibit at left 3000  $\text{cm}^{-1}$  regions. The C-H aliphatic stretching exhibit at right 3000  $\text{cm}^{-1}$  regions. The C-H in-plane ring bending exhibit at 1300-1000  $\text{cm}^{-1}$ . The C-H out-of-plane ring-bending exhibit at 900-690  $\text{cm}^{-1}$ .



The N-H bending often are covered the (C=C) bands of aromatic compounds at same region. The (C=C) aromatic stretching exhibit as doublet at  $1590\text{ cm}^{-1}$ ,  $1475\text{ cm}^{-1}$ .

The C-H bending isopropyl group of 3-cyano-6-isopropyl-2(1H)-pyridone is slit to equivalent doublet at  $1375\text{ cm}^{-1}$  region.

$^1\text{H}$  NMR spectra of the chromium paramagnetic complexes are not clear. By contraries,  $^1\text{H}$  NMR spectra of the chromium(II) diamagnetic complexes are clear, whereby, the quadruple bond between dichromium in these complexes are formed.

$^1\text{H}$  NMR spectra results of 3-cyano-2(1H)-pyridone derivatives and their complexes with Cr(II) are as follow:

H(3-CN)mhp:  $^1\text{H}$  NMR ( $\text{DMSO-}d_6 + \text{CDCl}_3$ ):  $\delta$  2.26 (s, 3H, Me), 6.18 (d,  $J = 7.5\text{ Hz}$ , 1H, H-5), 8.03 (d,  $J = 7.5\text{ Hz}$ , 1H, H-4), 12.53 (bs, 1H, NH).

$\text{Cr}_2[(3\text{-CN})\text{mhp}]_4 \cdot \text{H}_2\text{O}$ :  $^1\text{H}$  NMR ( $\text{DMSO-}d_6$ ):  $\delta$  2.49 (s,  $\text{H}_2\text{O}$ ), 2.50 (s, 3H, Me), 7.19 (d, 1H, H-5), 8.996 (d, 1H, H-4).

The hydrogen's resonance of these complexes is shifted to downfield and the chemical shift increases. Thus 3-cyano-2(1H)-pyridone derivatives ligands are coordinated to chromium, whereby, electron density on ring decreases. The hydrogen resonance of the ring nitrogen are omitted in the  $^1\text{H}$  NMR spectra of all complexes that show the ring nitrogen of these complexes are coordinated to chromium as  $\text{N}^-$ .

The fourth hydrogen's of  $\text{Cr}_2[(3\text{-CN})\text{mhp}]_4 \cdot \text{H}_2\text{O}$  are appeared in the  $^1\text{H}$  NMR spectra of complexes, whereby, the structures of these complexes are close to isostructural, approximating to  $\text{D}_{2d}$  symmetry. The (Cr-N) and (Cr-O) bands are trans to their own kind, thus leading to overall  $\text{D}_{2d}$  symmetry.

Attention to clear  $^1\text{H}$  NMR spectra of complex, quadruple bond between dichromium are confirmed in these synthesized complexes. By attention into elementary analysis results, one can see the reliable coincidence between the experimental and theory per cent, whereby, L:M attribution are 4:2 in complexes and  $\text{H}_2\text{O}$  exist in the complexes structure. UV-Vis spectra of the  $\text{Cr}^{2+}$  complexes  $\text{M}_2(\text{Xhp})_4$  show three distinct regions<sup>10,11</sup>.

An  $\alpha$  region [ $22320\text{ cm}^{-1}$  or  $448\text{ nm}$  ( $\epsilon = 480\text{ M}^{-1}\text{ cm}^{-1}$ )], which has been attributed to a  $\sigma\text{-}\sigma^*$  transition and often exhibits a vibrational fine structure due to the M-M stretch, a  $\beta$  region ( $24815\text{ cm}^{-1}$  or  $402\text{ nm}$  ( $\epsilon = 285\text{ M}^{-1}\text{ cm}^{-1}$ )) region attributed to a  $\sigma\text{-}\pi^*$  transition and a  $\gamma$  region above  $34000\text{ cm}^{-1}$  which is ligand based and has high extinction coefficient (above  $23000\text{ cm}^{-1}$ ).

UV-Vis spectra results of the 3-cyano-2(1H)-pyridone derivatives in DMF are listed in Table-7.

The M-M bond distances reported were 1.87(3), 2.065(1), 2.161(1) Å for the iso structural chromium, molybdenum, tungsten dimers. Therefore, it is not surprising that the lowest energy electronic transitions are regular

TABLE-7  
UV-VIS SPECTRA RESULTS OF THE 3-CYANO-2(1H)-PYRIDONE  
DERIVATIVES IN DMF

Complex	$\alpha$ region:	$\beta$ region:	$\gamma$ region
	$\lambda_{\max}$ (nm), ABS	$\lambda_{\max}$ (nm), ABS	
1	415, 3.126	369, 2.130	Higher energy
2	430, 3.125	384, 1.935	Higher energy
3	425, 3.126	379, 2.125	Higher energy
4	408, 3.123	360, 1.922	Higher energy
5	402, 3.124	356, 1.927	Higher energy

in both their energy and their intensity. The  $\sigma \rightarrow \sigma^*$  energies are 22470, 20160, 18000  $\text{cm}^{-1}$  for the chromium, molybdenum, tungsten dimers in  $M_2(\text{mhp})_4$  ( $M = \text{Cr}, \text{Mo}, \text{W}$ ) complexes<sup>12</sup>. Thus, the Cr-Cr bond distances row in the synthesized complexes are decreased as follow:  $2 > 3 > 1 > 4 > 5$

By the results of  $^1\text{H}$  NMR, FT-IR, UV-Vis spectra and elementary analysis of the complex, its structures are confirmed. Fig. 4 shows The structure of 3-cyano-2(1H)-pyridone derivatives complex as suggested by Cotton<sup>9</sup>.

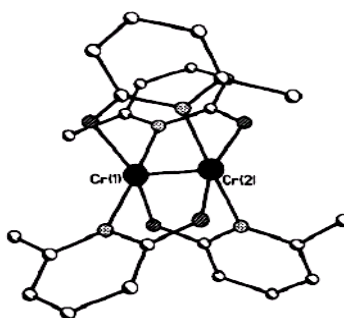


Fig. 4. Structure of 3-cyano-2(1H)-pyridone derivatives complex

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(Received: 5 June 2006;

Accepted: 21 April 2007)

AJC-5580