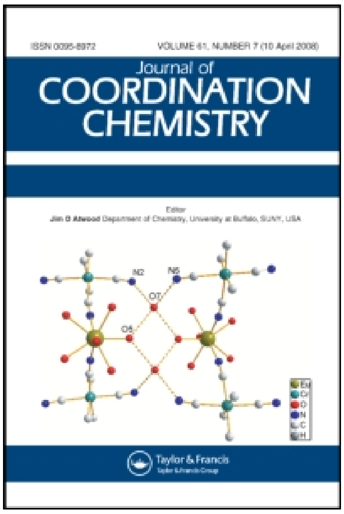


Journal of Coordination Chemistry

Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713455674

Preparation and Identification of a New [$Cr_2(NTA)_2(\mu\text{-}OH_2)$]·$2H_2O$ Complex

E. R. Souaya[a]; W. G. Hanna[a]; N. E. Milad[a]; E. H. Ismail[a]
[a] Department of Chemistry, Faculty of Science, Ain Shams University, Egypt

To cite this Article Souaya, E. R. , Hanna, W. G. , Milad, N. E. and Ismail, E. H.(2002) 'Preparation and Identification of a New [$Cr_2(NTA)_2(\mu\text{-}OH_2)$]·$2H_2O$ Complex', Journal of Coordination Chemistry, 55: 9, 999 — 1007
To link to this Article: DOI: 10.1080/0095897021000009965
URL: http://dx.doi.org/10.1080/0095897021000009965

J. Coord. Chem., 2002, Vol. 55(9), pp. 999–1007

PREPARATION AND IDENTIFICATION OF A NEW $[Cr_2(NTA)_2(\mu\text{-}OH_2)] \cdot 2H_2O$ COMPLEX

E.R. SOUAYA, W.G. HANNA*, N.E. MILAD and E.H. ISMAIL

Department of Chemistry, Faculty of Science, Ain Shams University, Egypt 11566

(Received 8 March 2001; Revised 28 June 2001; In final form 31 October 2001)

$[Cr_2(NTA)_2(\mu\text{-}OH_2)] \cdot 2H_2O$ is prepared by heating nitrilotriacetic acid (H_3NTA) with an aqueous suspension of freshly precipitated $Cr_2O_3 \cdot nH_2O$. Elemental analysis, IR spectra, UV/vis spectra, X-ray diffraction, thermogravimetric analysis, mass spectra and magnetic susceptibility measurements suggest the existence of a Cr–Cr bond. One of the three water molecules acts as a bridging ligand ($\mu\text{-}H_2O$) while the other two are waters of crystallization.

Keywords: Synthesis; Characterization; [Chromium (III)-nitrilotriacetate] complex

INTRODUCTION

Although metal complexes of nitrilotriacetic acid (H_3NTA) receive much attention in medical, biological and environmental studies, no definitive verification for their role is given. Ten transition metals are classified as trace metals required for life processes, Fe, Cu, Mn, Zn, Co, Mo, Cr, Sn, V and Ni [1]. Each transition metal catalyzes a specific reaction in nature and has a unique function. Lately, chromium received much attention due to its biological activity [2], which covers a variety of fields, the most important of which is Cr(III) therapy to help reduce the insulin requirement in hypoglycemic diabetes [3,4]. Chromium ions and others such as cadmium and zinc also activate protein kinase [5].

Such important applications require carrying out chemical studies which may help in clarifying the role played. The general formula of most metal-NTA complexes predicts a 1 : 1 metal to NTA ratio, but relatively little is known about the exact geometry of these complexes [6]. The H_3NTA ligand normally acts as a quadridentate ligand in most of these complexes, binding with a nitrogen atom and three carboxylate oxygens to the metal ion, but the exact nature of the two ligands which occupy the other two bonding sites to complete the octahedral geometry, are less studied. These two bonding sites are occupied by H_2O and OH^- in α- and β-$K[Co(NTA)(H_2O)(OH) \cdot H_2O$ complexes [7]. A crystal study, however, proved that in $Cs_2[Co_2(NTA)_2(\mu\text{-}OH)_2 \cdot 4H_2O$, the two sites are occupied by two OH^- ligands [8].

---

*Corresponding author. E-mail: wageih@hotmail.com

ISSN 0095-8972 print: ISSN 1029-0389 online
DOI: 10.1080/0095897021000009965

Little structural and synthetic work was done on [Cr(III)-NTA] complexes compared to the cobalt analogues. Uehara *et al.* [9] obtained the complex $[Cr(NTA)(OH)(H_2O)_2]^-$ where the NTA ligand is coordinated through its three carboxylate oxygens. A ^{1}H NMR study of the complexes prepared by Uehara *et al.* [9] proved that these complexes are actually tetracoordinated NTA complexes [10]. Uncertainty about the exact geometry of [Cr-NTA] complexes, led us to undertake the present study in an attempt to characterize the Cr-NTA complex in both the solid state and in an aqueous solution.

EXPERIMENTAL

Materials

All chemicals used were of analytical grade (AR) and products of Aldrich (USA).

Preparation of $Cr_2(NTA)_2 \cdot 3H_2O$

Excess of freshly precipitated $Cr(OH)_3$ was prepared by dissolving (4.80 g, 0.01 M) chromium alum in 30 mL of H_2O and adding 2.0 mL of ammonia solution (25% m/m) in a dropwise manner. The blue-green precipitate $\{Cr_2O_3 \cdot nH_2O\}$ was separated from the solution by centrifuge. This hydrous chromic oxide $\{Cr_2O_3 \cdot nH_2O\}$ was confirmed by the "*d*" line of the X-ray crystallography corresponding as reported in ASTM cards (Table II). Nitrilotriacetic acid $\{H_3NTA\}$ (1.91 g, 0.01 M) and the freshly prepared precipitate were suspended in water (40 mL) and heated to boiling for about fifteen minutes. The reaction mixture was then cooled, filtered and allowed to evaporate gently on a water bath for several hours until the volume is greatly reduced (5 mL). The residues was dissolved in 20 mL warm H_2O and filtered, the volume was greatly reduced again (5 mL). The pH of the blue-violet filtrate was found to equal 3.0. The filtrate was then allowed to stand for several days. The blue-violet crystals of a [Cr-NTA] complex were separated and recrystallized in H_2O. The crystals were filtered through a No. 2 sintered glass crucible, washed with 96% ethyl alcohol and ether and kept in a vacuum desiccator over silica gel. The yield is 1.0 g (37%).

Apparatus

Microanalysis of C,H,N was performed with a Perkin-Elmer 2400 CHN analyzer. Chromium was determined by AAS using a Perkin-Elmer AAS 3100 apparatus.

Molar conductance measurements were performed in double distilled water using WT WΔ 812 Weilheium conductivity meter, model LBR, fitted with a cell model LTA 100.

Thermogravimetric analysis was carried out on a Perkin-Elmer 7 series thermal analysis system, in a nitrogen atmosphere at a heating rate of 10°C/min^{-1}.

Magnetic susceptibilities were measured by the Gouy's method at room temperature using a magnetic susceptibility balance (Johnson Mathey), Alfa product, Model No. (MKI). Diamagnetic corrections were calculated from Pascal constants. $Hg[Co(SCN)_4]$ was used as a standard.

Mass spectra were recorded at 350°C and 70 eV on a GL/MS Finniganmat SSQ 7000 apparatus.

FTIR spectra were recorded on a Perkin-Elmer spectrophotometer and Jasco model FTIR spectrophotometer using KBr discs in the 4000–400 cm^{-1} and CsI discs in the 500–200 cm^{-1}.

Raman spectra were recorded on FTIR-Raman Spectra Jasco 620 model.

X-ray diffraction patterns (XRD) of the prepared solid complex were recorded using a Philips X-ray diffractometer model PW 1140/90 and Fe-filtered CuK_α radiation.

UV/vis spectra were measured at room temperature on a Jasco model V-550 UV/vis spectrophotometer.

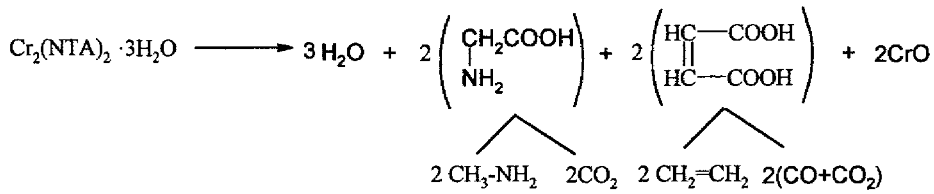
RESULTS AND DISCUSSION

Structure of the Solid Complex

The presence of $Cr_2O_3 \cdot nH_2O$; or $\{Cr(OH)_3\}$, over H_3NTA in the method of preparation excludes the possibility of formation of any complex other than the 1 : 1.

Thermogravimetric Analysis

The thermograph of the complex (Fig. 1) shows inflections which can be illustrated as follows:



$$Cr_2(NTA)_2 \cdot 3H_2O \longrightarrow 3H_2O + 2\begin{pmatrix} CH_2COOH \\ NH_2 \end{pmatrix} + 2\begin{pmatrix} HC{-}COOH \\ \| \\ HC{-}COOH \end{pmatrix} + 2CrO$$

$$2\,CH_3\text{-}NH_2 \quad 2CO_2 \quad 2\,CH_2{=}CH_2 \quad 2(CO+CO_2)$$

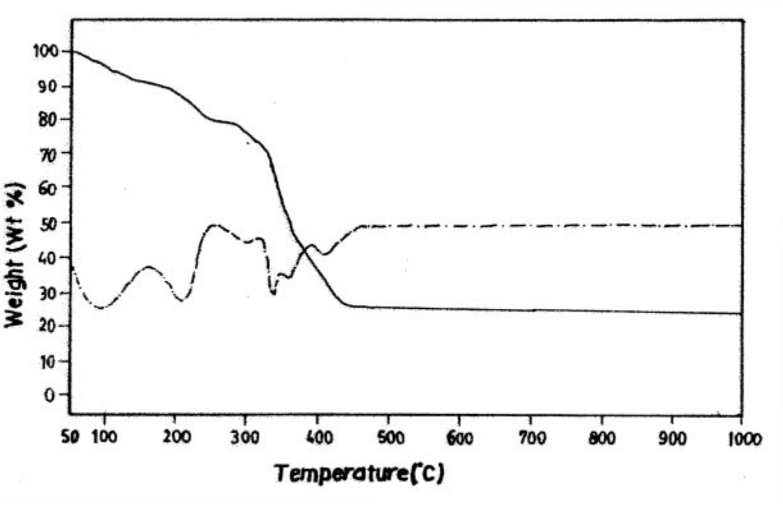


FIGURE 1 The thermograph (TG and DTG) of the $[Cr_2(NTA)_2(\mu\text{-}OH_2)] \cdot 2H_2O$ complex.

Examination of the thermograph of this complex reveals that the complex dissociated in six successive steps (Table I), which are: (i) The temperature ranges 30–170°C {evolution of crystalline and bridge water molecules}. (ii) The temperature ranges 170–245°C {decomposition of complex and evolution of two $–CH_2–N=$fragments}, and at 245–320°C {evolution of two $–CH_2=CH_2–$fragments}. (iii) The temperature ranges 320–345, 345–385, and 385–460°C {evolution of two molecules of CO then followed by two molecules of CO_2 for the other steps}. A slow weight loss took place at the first two steps followed by very rapid weight loss. The slow weight losses began in the temperature range 30–320°C, while the more rapid change took place in the range 320–460°C. The first weight losses were due to the loss of aquo ligands and the decomposed NTA ligands, which decomposed to the $–CH_2–N=$ group followed by $–CH_2=CH_2–$ group. (iv) The percent weight of the remaining chromium oxide after complete thermal decomposition of the complex is equal to 25.5%. This white chromium (II) oxide is formed due to the reductive CO gas evolved during the decomposition of the complex in an inert N_2 atmosphere. The white CrO was confirmed by its changing to green chromium (III) oxide when heated in an air atmosphere, and the "*d*" line of the X-ray crystallography corresponding to Cr_2O_3 as reported in ASTM cards (Table II). This thermogravimetric analysis together with the elemental analysis shown below is sufficient to suggest a molecular formula of $[Cr_2(NTA)_2OH_2]\cdot 2H_2O$.

	Cr	C	H	N%
Calcd.	19.48	27.06	3.37	5.24
Found	19.50	26.55	3.48	5.47

TABLE I Thermal analysis for $[Cr_2(NTA)_2(\mu\text{-}OH_2)]\cdot 2H_2O$ complex

Step	*Temp. range* °C	*Total loss (%)*	*Different loss, %Found (Calcd.)*	*Fragments lost*	(T_d)°C	*Fragments lost*
I	30–170	10.0	10.0 (10.1)	$–3H_2O$	92	H_2O molecules
II	170–245	20.5	10.5 (10.5)	$2–CH_2N–$	210	Methyl amino group fragment
III	245–320	30.8	10.3 (10.5)	$2–CH_2=CH_2–$	302	Ethylene group fragment
IV	320–345	41.6	10.8 (10.5)	–2CO	335	Carbon monoxide group
V	345–385	58.0	16.4 (16.5)	$–2CO_2$	358	Carbon dioxide group
VI	385–460	74.5	16.5 (16.5)	$–2CO_2$	409	Carbon dioxide group
		Total loss = 74.5%	Total loss = 74.5 (75.6)%			Remaining materials (2CrO) = 25.5 (25.4)%

TABLE II X-ray diffraction data of $[Cr_2(NTA)_2(\mu\text{-}OH_2)]\cdot 2H_2O$ complex, chromium(III) oxide (Cr_2O_3), and hydrous chromic oxide ($Cr_2O_3\cdot nH_2O$)

$[Cr_2(NTA)_2(\mu\text{-}OH_2)]\cdot 2H_2O$ $d\ (10^{-1}\ nm)_{Intensity}$	Cr_2O_3 $d\ (10^{-1}\ nm)_{Intensity}$	*Hydrous chromic oxide* $d\ (10^{-1}\ nm)_{Intensity}$
$2.49_{100\%}$	$2.67_{100\%}$	$4.90_{100\%}$
$2.66_{70\%}$	$2.48_{95\%}$	$3.38_{100\%}$
$3.66_{65\%}$	$1.67_{90\%}$	$2.90_{60\%}$
$1.67_{65\%}$	$3.63_{70\%}$	$2.34_{60\%}$
$2.18_{40\%}$	$1.43_{40\%}$	$2.19_{40\%}$

Magnetic Susceptibility Measurements

The magnetic moment of the complex, 2.87 BM at 301 K, corresponding to two unpaired electrons per chromium (III), suggests a dimeric complex with a single Cr–Cr bond. The alcoholate ligand has a pronounced tendency to form a bridged chromium (III) dimer [12]. The susceptibility of $[Cr(pyridine\text{-}N\text{-}oxide)_6](ClO_4)_3$ has been reported to obey the Curie-Weiss law [13]. No one has yet prepared large single crystals of this complex, nor has its crystal structure been reported, therefore we offer this complex for other scientists to begin study of its low-temperature magnetic measurements.

Mass Spectrum

Examination of the mass spectrum shows (Fig. 2) a molecular ion beam of very low intensity at 534 m/e corresponding to the molecular formula $[Cr_2(NTA)_2(\mu\text{-}OH_2)\cdot 2H_2O$. It is well known that molecular weights can be determined directly, even to ten thousands of a mass unit on more sophisticated spectrometers. The dimeric nature of the complex is confirmed by the very low conductivity value of the 10^{-3} M solution which was found to be 3.9 $ohm^{-1} cm^2 mol^{-1}$ indicating electrical neutrality. To satisfy the hexacoordination of chromium (III) in a distorted octahedral complex, one of the three water molecules is a bridging water while the other two are water of crystallization. Visser *et al.* [11] suggested the occurrence of μ-H_2O in the NTA complexes of Co [8] and Cr [11].

A mass spectrum of the complex [15] shows the molecular ion peak at m/e 250 (100%) which represents the half Mw of the dehydrated deuterated complex $[Cr_2(NTA)_2\cdot(\mu\text{-}OD_2)]$ i.e., $\frac{1}{2}(498+2)=250$. Stable fragments of Mw = 222 (20%) and 206 (31%) are shown on further decomposition and elimination of CO and CO_2. The intense molecular ion peaks at 268 (17%) represents half the Mw of the whole complex $[Cr_2(NTA)_2(\mu\text{-}OD_2)\cdot 2H_2O$ $\{\frac{1}{2}(534+2=268)\}$. Unequal fragmentation of the complex gives [Cr(NTA)] with Mw 240 (0.7%) and $[Cr(NTA.OD_2)]\cdot 2H_2O$ with Mw 296 (2.7%), the later fragment on further decomposition and elimination

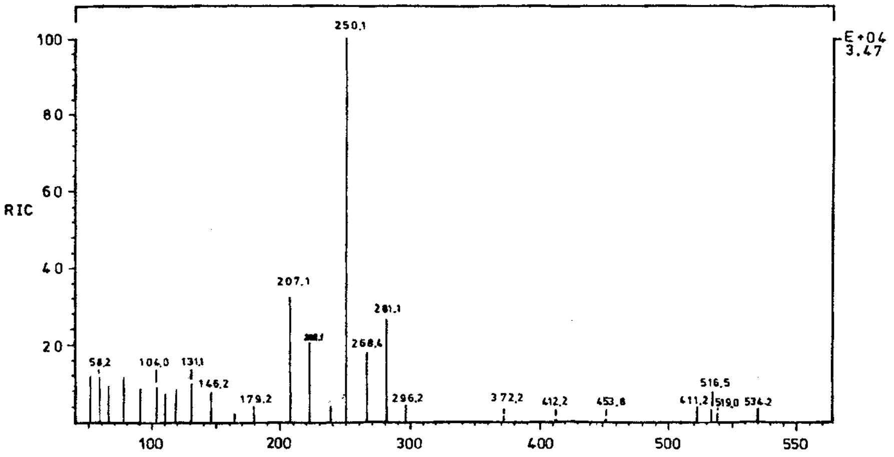


FIGURE 2 The mass spectrum of $[Cr_2(NTA)_2(\mu\text{-}OH_2)]\cdot 2H_2O$ complex.

{$CO+CO_2+H_2O$} gives a molecular ion peak at *m/e* 206 (31%). Other medium intense ion peaks appear on complete decomposition e.g., *m/e* at 104 (9%) which represents ($2CO_2+CO$), m/e at 58 (11%) which represents $-CH_2COO$, *m/e* at 132 (9%) which represents $-N{=}(CH_2COO)_2$ and m/e at 146 (7%) which represents $[-N{=}(CH_2COO)]_2$.

FTIR and Raman Spectra

Tomito and Ueno have studied the IR spectra of metal complexes of NTA and concluded that NTA acts as a quadridentate ligand in many complexes [17]. The bands of interest in the infrared spectrum of nitrilotriacetic acid are those at 3041 and 1733 cm^{-1} which are attributed to intramolecular hydrogen bonding and the presence of undissociated carboxylic groups respectively. The IR spectrum of the chromium complex under investigation (Fig. 3) shows the disappearance of these two bands which suggests that none of the carboxylates is present in the undissociated form. The bands at 1640 and 1734 cm^{-1} are those for the stretching frequencies of –COO– and COOH. The presence of a broad band at 3400 cm^{-1} confirms our postulate that we are dealing with a hydrated complex. In Raman spectra of several solids known to contain hexaaquo ions a strong polarized band has been observed near 404 cm^{-1}, this is assigned to ν(M–OH$_2$) [15]. The bands at 552 and 411 cm^{-1} are those for Cr–N and Cr–O bonds.

Finally the presence of intense Raman active bands (Fig. 4) may be taken as a support for the presence of a Cr–Cr bond. Complexes of chromium containing a Cr–Cr bond show a Raman band at $\approx$160 cm^{-1} [14], and it is observed that the presence of bridging groups shifts the M–M band to higher values. This justifies our assumption of assigning the Raman band at 200 cm^{-1} to a Cr–Cr bond.

X-ray Diffraction Spectra

X-ray patterns of the prepared solid $[Cr_2(NTA)_2(\mu\text{-}OH_2)]\cdot 2H_2O$ complex were taken over the range of $2\theta = 6 - 60°$ (Fig. 5). The principal "*d*" lines and their intensities

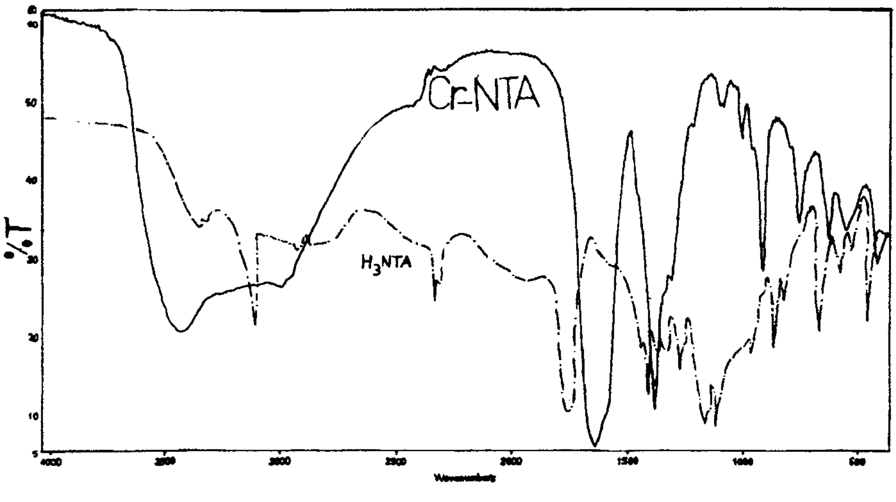


FIGURE 3 The FTIR spectra of the (H_3NTA) ligand and $[Cr_2(NTA)_2(\mu\text{-}OH_2)]\cdot 2H_2O$ complex.

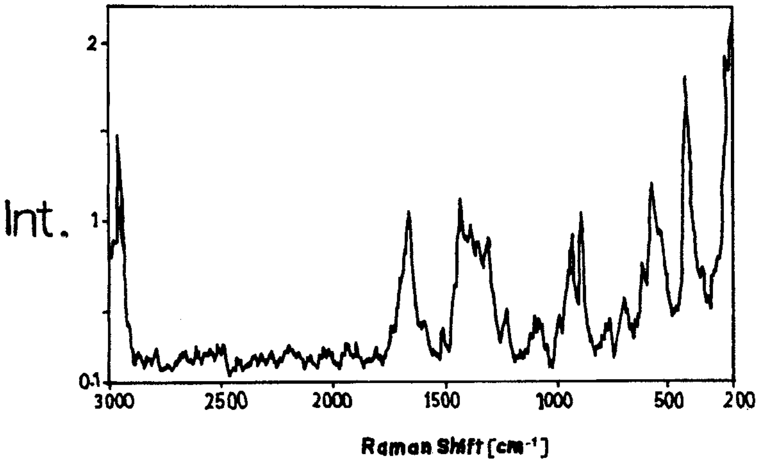


FIGURE 4 The Raman spectrum of $[Cr_2(NTA)_2(\mu\text{-}OH_2)]\cdot 2H_2O$ complex.

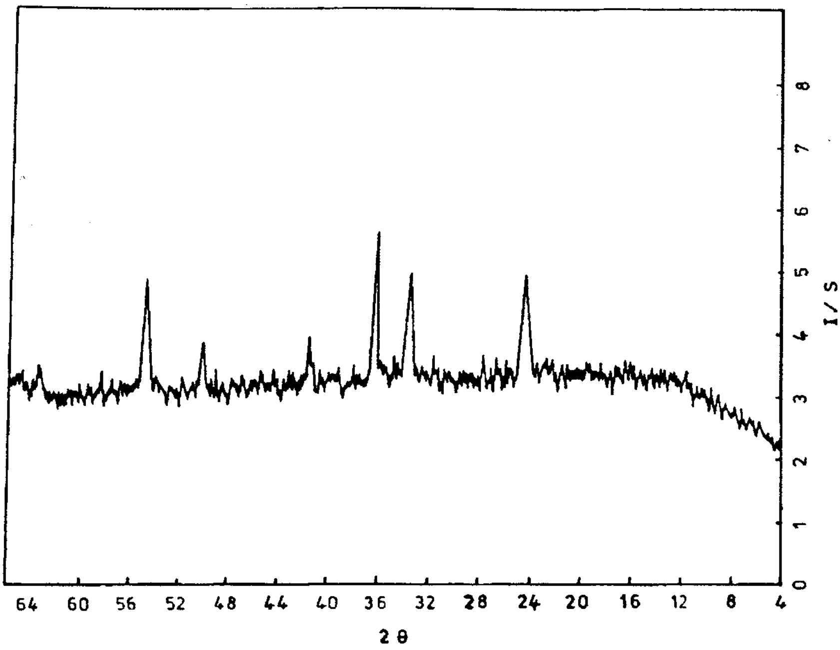


FIGURE 5 X-ray diffraction pattern (XRD) of the $[Cr_2(NTA)_2(\mu\text{-}OH_2)]\cdot 2H_2O$ complex.

are represented in Table II. The complex is a crystalline solid, characterized by a high degree of crystallinity, high symmetry and large size of unit cells.

Identification of Cr-NTA Species in Aqueous Solution

The crystal of the chromium complex was dissolved in H_2O and the UV/vis spectra were recorded (Fig. 6). The spectra of complex shows two absorption maxima at

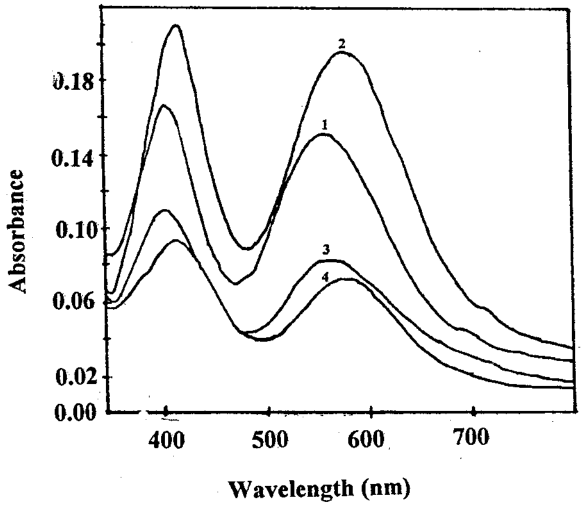


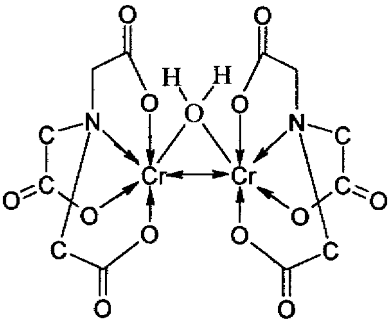
FIGURE 6 UV/vis spectra of different [Cr(III)-NTA] species in solution: (1) $[Cr_2(NTA)_2(\mu\text{-}OH_2)] + HCO_3^-$ at pH = 6–7; (2) $[Cr_2(NTA)_2(\mu\text{-}OH_2)]$ at pH = 3 (original complex); (3) $[Cr_2(NTA)_2(\mu\text{-}OH_2)] + H^+$ at pH = 1 and (4) $[CrCl_3 \cdot 6H_2O]$.

$\lambda_{max} = 406\,nm$ ($\varepsilon = 110\,M^{-1}\,cm^{-1}$) and λ_{max} 558 nm ($\varepsilon = 100\,M^{-1}\,cm^{-1}$) in agreement with the values of Visser *et al.* [11]. Crystals of $[Cr_2(NTA)_2(\mu\text{-}OH_2)] \cdot 2H_2O$ were dissolved in water (pH *ca.* 3) and the UV/vis spectrum recorded. $NaHCO_3$ was added to the solution (pH *ca.* 6–7) with no change in the absorption maxima. A fresh $[Cr_2(NTA)_2(\mu\text{-}OH_2)] \cdot 2H_2O$ solution ($10^{-3}\,M$) was prepared and UV/vis spectrum was recorded, (**2**) in Fig. 6. Spectrum (**1**) was recorded in acidic solution ($10^{-3}\,M$ in 0.1 M HCl). The addition of base (solid $NaHCO_3$) to the solution in (**1**) resulted in no change to the spectrum (**3**). Addition of acid to this solution resulted in the same spectrum as recorded in (**2**).

These results clearly point to a stable $[Cr_2(NTA)_2(\mu\text{-}OH_2)]$ complex in both acidic and alkaline solution. A comparison spectrum was made for this complex with aquo chromium (III) complex $[CrCl_3 \cdot 6H_2O](10^{-3}\,M)$. The spectra of aquo chromium complex (**4**) shows two absorption maxima at λ_{max} 668 nm (ν_1) assigned to $^4A_{2g} \rightarrow {}^4T_{2g}$ transition (ν_1 corresponds to 10 Dq; CT band) and $\lambda_{max} = 408\,nm$ (ν_2) assigned to $^4A_{2g} \rightarrow {}^4T_{1g}(F)$ transition. The $^4A_{2g} \rightarrow {}^4T_{1g}(P)$ transition (ν_3) was expected to be seen but this absorption maximum was not realized under these experimental results. This may be due to the delocalization of the metal electron over molecular orbital that encompasses not only the metal but the ligand as well (nephelauxetic effect) [16]. Comparing the spectrum of aquo chromium (III) complex with our complex, we can conclude that the band at $\lambda_{max} = 406\,nm$ represents the $^4A_{2g} \rightarrow {}^4T_{1g}$ (F) transition and λ_{max} 558 nm represents the $^4A_{2g} \rightarrow {}^4T_{2g}$ transition (ν_1 corresponds to 10 Dq; CT band) [18].

CONCLUSION

From conductometric measurements, elemental analyses, thermal analysis, magnetic moment, XRD, mass, IR, Raman, and UV/vis spectra, one can conclude that the distorted octahedral structures (monoclinic crystal system) for $[Cr_2(NTA)_2(\mu\text{-}OH_2)]\cdot 2H_2O$ complex will be:



References

[1] J. Andrew and Ge J.M. Samete (1999). *Metals and Air Pollution Particles*. Academic Press. Ltd., UK.
[2] J.W.H. Mali, K. Malten and F.C.J. Van Neer (1966). *Arch. Dermatol*, **93**, 41.
[3] E. Mentasti, F. Sec and M. Venturin (1982). *Inorg. Chem.*, **26**, 602.
[4] J. Barrett, P. O'Brien and J.P. de Jesus (1985). *Polyhedron*, **4**, 1.
[5] M. Bagchi, L. Tang and S.J. Stohs (1997). *Toxicol Lett.*, **91**, 31.
[6] E.R. Souaya, W.G. Hanna, E.H. Ismail and N.E. Milad. (2000). *Molecules*, **5**, 1121.
[7] M. Mori, M. Shibata, E. Kyuno, and Y. Okulio, (1958). *Bull. Chem. Soc. Jpn.*, **31**, 940.
[8] H.G. Visser, W. Purcell, S.S. Basson and Q. Claasen (1996). *Polyhedron*, **16**, 285.
[9] A. Uehara, E. Kyuno and R. Tsuchiya (1967). *Bill. Chem. Soc. Jpn.*, **40**, 2317.
[10] N. Koine, J. Bianchini and J. Legg (1986). *Inorg. Chem.*, **25**, 2835.
[11] H.G. Visser, W. Purcell and S.S. Basson (1999). *Polyhedron*, **18**, 2795.
[12] M.H. Chisholm, F.A. Cotton and E.G. Horvater (1979). *Z. Anorg. Chem.*, **449**, 41.
[13] R.L. Carlin, R. Burriel, J. Pone and J. Casabo (1983). *J. Inorg. Chem.*, **22**, 2832.
[14] N.A.D. Carry and H.C. Clark, (1967). *Chem. Comm.*, 292.
[15] E. De Hoffmann, J. Charette and V. Strobant (1996). *Mass Spectrometry Priniciples and Application*. John Wiley and Sons Ltd., Chichester, England.
[16] I. Nakagawa and T. Shimanouchi (1964). *Spectrochim. Acta.*, **20**, 429.
[17] Y. Tomito and K. Ueno (1963). *Bull. Chem. Soc. Jpn.*, **36**, 1069.
[18] A.F. Cotton, G. Wilkinson, C.A. Murillo and M. Bochmann (1999). *Advanced Inorganic Chemistry*. 6th Edition. Wiley Interscience Publication, New York, USA.