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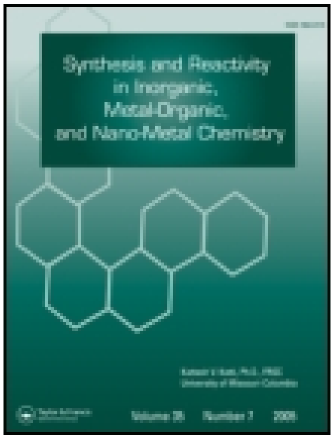

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SYNTHESIS AND CHARACTERIZATION OF MONONUCLEAR AND BINUCLEAR CHROMIUM(III) COMPLEXES OF α-BENZOIN OXIME

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SYNTHESIS AND CHARACTERIZATION OF MONONUCLEAR AND BINUCLEAR CHROMIUM(III) COMPLEXES OF α-BENZOIN OXIME

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ABSTRACT

Irradiation of a THF solution containing $Cr(CO)_6$ and α-benzoin oxime (H_2BNO) under various atmospheric conditions, of either argon or vacuum, gave two dichromium(III) complexes of the formulae $[Cr(\mu\text{-}OH)(BNIM)(HBNO)]_2$ (**1**) and $[Cr(BNIM)(HBNO)(THF)]_2O$ (**2**) where BNIM is the α-benzoin imine radical anion formed as a result of homolytic cleavage of the oxime N-OH bond. When a related reaction of α-benzoin oxime was carried out with $Cr(NO)_3$ in open atmosphere, $Cr(HBNO)_3$ (**3**) was obtained. Variable-temperature magnetic susceptibility measurements show a magnetic moment of 8.12 B.M. for the μ-dihydroxo complex (**1**) at room temperature. This high magnetic moment value strongly confirms the formulation of a dimer consisting of two benzoin imine radicals ($S = 1/2$ coordinated to bridged dichromiu-

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m(III) (S = 3/2) ions. In contrast, the μ-oxo complex (**2**) shows a magnetic moment of 3.10 B.M. which is even smaller than that observed for the monomeric complex $Cr(HBNO)_3$ (**3**) at room temperature. Moreover, IR spectral analysis was very informative in assigning the vibrations due to $Cr_2(OH)_2{}^{4+}$ and Cr_2O^{4+} moieties for the complexes (**1**) and (**2**), respectively. Thermal gravimetric analysis (TGA) of complex (**2**) has shown decompositions due to coordinated THF molecules, followed by gradual decomposition of bezoin imine ligands. Interestingly, a low-energy transition in the Vis-near-IR region assigned as BNIM → Cr(III) LMCT transition was observed for the $[Cr(BNIM)(HBNO)(THF)]_2O$ complex.

INTRODUCTION

Transition metal complexes containing paramagnetic organic ligands, such as semiquinones[1,2], mono-oximes[3,4] and diimines[5–7] are of great interest because of their redox and magnetic properties. The unique magnetic properties displayed by these complexes result from antiferromagnetic or ferromagnetic metal-ligand and/or ligand-ligand exchange interactions, demonstrating the radical characters of the paramagnetic ligand[2]. Moreover, dimeric complexes containing paramagnetic metal and ligand centers, *e.g.*, $[Fe(\mu\text{-}OMe)(DBSQ)_2]_2$, (DBSQ = di-*tert*-butyl-1,2-benzosemiquinone) show a complicated magnetic behavior that results from the coupling effects of Fe-SQ, SQ-SQ and Fe-Fe exchange interactions[8].

Recently, there has been a growing interest in the coordination chemistry of oximes with transition metals[9–13], which stems from their utilization in a wide range of applications. There are several examples in the chemical literature of the uses of oximes as analytical reagents[14–16], and their complexes as models for biological systems[17,18]. In addition, an α-benzoin oxime complex of copper(II) is used in industry for the formation of non-silver photographic images[19].

As most of the work on oxime complexes has been performed with transition metal salts, in this paper we report the first reactions between α-benzoin oxime (H_2BNO) and $Cr(CO)_6$. These reactions result in the formation of two new dimeric chromium(III) complexes, $[Cr(\mu\text{-}OH)(BNIM)(HBNO)]_2$ (**1**) and $[Cr(BNIM)(HBNO)(THF)]_2O$ (**2**) have been obtained as stable solids. They represent a new addition to the oxime coordination chemistry of chromium, and to complexes consisting of a radical ligand (S = 1/2) coordinated to bridged Cr(III) (S = 3/2) metal ions, and offers an opportunity to study the magnetic behavior that may result from the spin interactions between Cr-BNIM and Cr-Cr centers. Furthermore, the complexes were designed to contain various bridging ligands (μ-oxo and μ-dihydroxo), connecting the two Cr(III)(BNIM) units, to control the magnitude of magnetic interactions between these units. We also describe the synthesis and characterization of the monomeric tris-complex, $Cr(HBNO)_3$. This compound, that does not contain a benzoinimine radical, has offered useful information for the structure, electronic and magnetic characterizations of the dimeric complexes.

EXPERIMENTAL

Materials

Chromium hexacarbonyl, $Cr(CO)_6$, and chromium(III) nitrate, $Cr(NO_3)_3$, and α-benzoin oxime were used as received from Aldrich. Solvents were purified by distillation: tetrahydrofuran from sodium benzophenone; petroleum ethers from sodium hydride; chloroform from P_4O_{10}; ethanol from magnesium ethoxide.

Physical Measurements

Variable-temperature (20–298K) magnetic susceptibility data were obtained with an Oxford Faraday magnetometer. Diamagnetic corrections were estimated from Pascal's constants to obtain the corrected molar paramagnetic susceptibilities of the compounds (χ_M^{corr})[20,21]. The magnetic moments were calculated by the equation $\mu_{eff} = 2.828\ (\chi_M^{corr}.T)^{1/2}$. Infrared spectra (4000–400 cm^{-1}) were recorded as KBr pellets on a Unicam Mattson 1000 FTIR spectrometer. The electronic absorption spectra were recorded by using a model 1601 Shimadzu spectrometer. Samples of $4\text{–}6 \times 10^{-6}$ M concentrations in DMF were measured against the solvent in the reference cell. Elemental analyses were performed using a Perkin-Elmer 2400 CHN elemental analyzer. Mass spectra were obtained on a Finnigan MAT SSQ 7000 mass spectrometer. Thermal gravimetric analyses (TGA) were carried out under nitrogen with a heating rate of 10 °C/min. using a Perkin-Elmer thermal analyzer.

Complex Syntheses

$[Cr(OH)(BNIM)(HBNO)]_2$ (**1**)

$Cr(CO)_6$ (0.13 g, 0.59 mmol) and α-benzoin oxime (0.30 g, 1.32 mmol) were dissolved in 50 mL of degassed tetrahydrofuran under argon. The solution was irradiated for 48 h with an UV-lamp and heated in a paraffin oil bath at 70 °C. The solution which was initially colorless changed to yellow and finally to brown. During the reaction strong effervescence was observed. The volume of the brown solution was reduced with a flow of argon gas. Fine, dark brown crystals of the complex were obtained in 0.14 g (48%) yield. Anal. Calcd for $C_{56}H_{48}N_4O_8Cr_2$ (MW 1009.01): C, 66.66; H, 4.79; N, 5.55. Found: C, 66.31; H, 4.54; N, 5.58. Mass spec. M/z (p^+), 1012. M. p. decomp >160 °C.

$[Cr(BNIM)(HBNO)(THF)]_2O$ (**2**)

α-Benzoin oxime (0.20 g, 0.88 mmol) and $Cr(CO)_6$ (0.12 g, 0.54 mmol) were mixed in 50 mL tetrahydrofuran. The mixture was irradiated with an UV-lamp and heated in a paraffin oil bath at 70 °C under reduced pressure for 3 days. Evaporation of the solvent resulted in a yellow-brown solid. Fine crystals of $[Cr(BNIM)(HBNO)(THF)]_2O$ were obtained by crystallization from $CHCl_3$. The crystals were washed several times with petroleum ether (bp. 40–60 °C). The product was obtained in 0.17 g (67%) yield. Anal. Calcd for $C_{64}H_{62}N_4O_9Cr_2$ (MW 1135.2): C, 67.71; H, 5.50; N, 4.93. Found: C, 67.55; H, 5.39; N, 4.60. Mass spec. M/z (p^+), 1136. M. p. decomp > 80 °C.

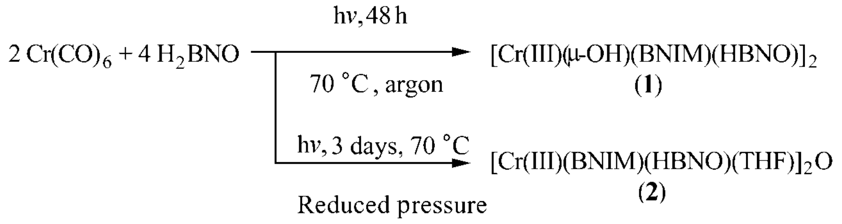
$Cr(HBNO)_3$ (**3**)

A mixture of $Cr(NO)_3 \cdot 9H_2O$ (0.50 g, 1.64 mmol) and α-benzoin oxime (1.00 g, 4.4 mmol) was dissolved in 100 ml of THF-EtOH (3:1). The solution was heated at 70 °C for 2 h, then the volume of the resulting green solution was reduced. The green solid obtained was washed several times with hot petroleum ether (bp. 60–80 °C) and then recrystalized from ethanol. The green crystals of $Cr(HBNO)_3$ were obtained in 0.86 g (80%) yield. The complex was left to dry *in vacuo* for 2 h. Anal. Calcd for $C_{42}H_{36}N_3O_6Cr$ (MW 730.8): C, 69.03; H, 4.96; N, 5.75. Found: C, 68.57; H, 5.14; N, 5.60. Mass spec. M/z (p^+), 728. M. p. 187 °C.

RESULTS AND DISCUSSION

Reactions of oximes with Ni(II) have been used to study the oxidative addition to Ni(II) metal ions[22]. Recently, Hank *et al.*[11] have shown that a stoichiometric reaction of α-benzoin oxime with Ni(II) results in the formation of a stable Ni(IV)$(OH)_2(BNIM)_2$ complex. In addition, the coordinated OH is formed by the cleavage of the oxime N-OH.

In the present study under various atmospheric conditions two different complexes were prepared from the reaction of α-benzoin oxime and $Cr(CO)_6$. Irradiation of a solution containing chromium hexacarbonyl and α-benzoin oxime (H_2BNO) under an inert atmosphere of argon, yielded the μ-dihydroxochromium(III) dimer, $[Cr(III)(OH)(BNIM)(HBNO)]_2$ (**1**). While changing the reaction condition to reduced atmospheric pressure (i.e., under vacuum) resulted in the formation of the μ-oxo dimer, $[Cr(III)(BNIM)(HBNO)THF)]_2O$ (**2**) (eq. 1). The tris-derivative, $Cr(III)(HBNO)_3$, was prepared to aid in elucidating the structures of the other complexes by comparing their spectroscopic data. The tris-derivative was prepared by reacting α-benzoin oxime with $Cr(NO)_3$ in THF (eq. 2).



$$2\,Cr(CO)_6 + 4\,H_2BNO \xrightarrow[70\ ^\circ C,\ argon]{h\nu,\ 48\ h} [Cr(III)(\mu\text{-}OH)(BNIM)(HBNO)]_2\ (\mathbf{1})$$

$$2\,Cr(CO)_6 + 4\,H_2BNO \xrightarrow[Reduced\ pressure]{h\nu,\ 3\ days,\ 70\ ^\circ C} [Cr(III)(BNIM)(HBNO)(THF)]_2O\ (\mathbf{2})$$

(1)

$$Cr(NO_3)_3 + 3\,H_2BNO \xrightarrow[70\ ^\circ C,\ 2\ h]{reflux\ in\ air} Cr(HBNO)_3\ (3)$$

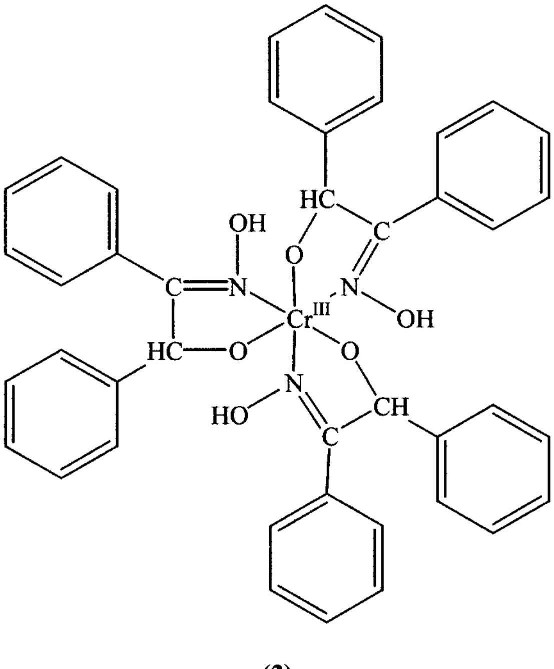
(2)

Infrared Spectra

Generally, oximes[23,24] are characterized by three IR absorption bands at 3300–3150 cm^{-1} (OH str.), 1690–1620 cm^{-1} (C=N str.), and ~950 cm^{-1} (N-O str.). In the present study the α-benzoin oxime ligand shows these bands at 3326, 1670 and 990 cm^{-1} due to OH, C=N and N-O stretching modes, respectively.

The infrared spectrum of the tris-complex, $Cr(HBNO)_3$ (**3**), reveals a strong-intensity band at 1549 cm^{-1} due to the C=N stretching vibration. This band has shifted by 121 cm^{-1} to lower frequency from the C=N stretching frequency of the parent ligand. This significant lowering in the stretching frequency evidently indicates the involvement of the oxime C=N in coordination. Such behavior was previously observed for chromium and copper complexes of oxime ligands[4,25]. In contrast, the bands corresponding to OH and N-O stretches, observed at 3360 and 1028 cm^{-1}, respectively, are slightly shifted to higher frequencies with respect to those of the α-benzoin oxime ligand. Furthermore, the absence of vibrations characteristic of free or coordinated[26] NO_3^- exclude them from the structure of the complex. On the basis of the above IR spectral studies, which are further supported by elemental analyses and mass spectroscopic data, the structure given in Fig. 1 is suggested for the tris-chromium(III) complex.

The IR spectral data for the two dimeric complexes (**1**) and (**2**), presented in Table I, are drastically different from that observed for the tris-complex (**3**). It is interesting that both complexes, (**1**) and (**2**), show two



(3)

Figure 1. Suggested structure for the tris-complex, Cr(III)$(HBNO)_3$.

Table I. Characteristic IR Absorption Bands of Chromium α-Benzoin Oxime Complexes

	IR data (cm^{-1})[a]							
Complex	ν(OH)	ν(C=N)	ν(C=C)	ν(NO)	ν(Cr-OH-Cr)	ν(Cr-O-Cr)	ν(M-N)	ν(M-O)
[Cr(μ-OH)(BNIM) (HBNO)]$_2$	3437 s,b	1535 m 1447 s	1607 s	1017 s	955 s	–	527 s	643 m
[Cr(BNIM)(HBNO) (THF)]$_2$O	3420 m,b	1544 m 1445 vs	1591 s	1005 s	–	739 s	527 s	654 s
Cr(HBNO)$_3$	3368 s,b	1549 s	1599 s	1028 m,b	–	–	542 s	687 w

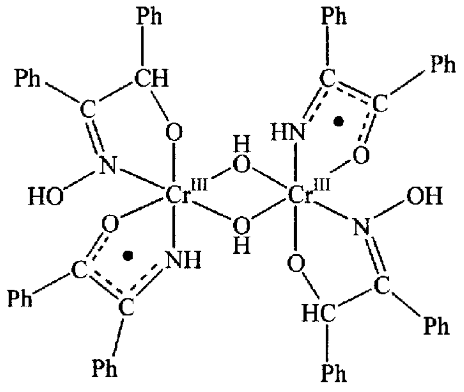
[a] w, weak; m, medium; s, strong; vs, very strong; b, broad.

bands in the characteristic range for the C=N stretching frequency. These bands are observed for complex (**1**) at 1535 and 1447 cm^{-1} and for complex (**2**) at 1544 and 1445 cm^{-1}. The first C=N band for both complexes is comparable to that observed for the tris-complex (**3**) at 1549 cm^{-1} while the second one is absent in the spectrum of both the tris-complex (**3**) and the free ligand and is assigned to the coordinated C=N stretching mode. Moreover, complex (**1**) displays a strong absorption band at 955 cm^{-1} which is unique among the spectra of the three chromium complexes. This band is assigned to a vibration mode associated with the $Cr_2(OH)_2^{4+}$ structural unit and suggests a dimeric complex in which the two chromium(III) metal ions are bridged by two OH groups. Our interpretion of the dihydroxo dimeric structure derives additional support from the fact that the infrared bands of $[Cr(pic)_2OH]_2$ and $[Fe(pic)OH]_2$ due to $Cr_2(OH)_2^{4+}$ and $Fe_2(OH)_2^{4+}$ are observed at 970 and 950 cm^{-1}, respectively[27]. On the other hand, the IR spectrum for complex (**2**) shows a strong absorption at 735 cm^{-1} which may be assigned to ν_{asym} of the Cr-O-Cr moiety and compares very well with that reported for several oxo-bridged complexes[28–30] in the range 730–745 cm^{-1}. Vibrations characteristic of coordinated THF are observed for complex (**2**) at 2957 and 2872 cm^{-1} (C-H str.) and 1119 cm^{-1} (vibration associated with C-O-C moiety). Consistent with this assignment (which is further supported by TGA), coordinated THF was reported[31–33] to show bands at 2950, 2860 and 1118 cm^{-1}.

It must be recalled that the second band due to C=N observed for both complexes (**1**) and (**2**) is assigned to C=N of an imine radical formed as a result of homolytic cleavage of the oxime N-OH bond by photolysis (Fig. 3). This interpretation is confirmed by magnetic studies of the complexes (vide infra) and gains further support from the IR data reported for chromium and molybdenum complexes containing oximate radicals[3,4]. These results, therefore, seem in conformity with the structures given in Fig. 2.

Magnetism

Magnetic exchange between paramagnetic metal ions and radical ligands of monomeric, dimeric and polymeric complexes has been a subject of several of our studies[8,33–36]. Variable-temperature (20–298K) magnetic susceptibility data were collected for complexes (**1**) and (**2**) as solids. Plots of the effective magnetic moment per molecule (μ_{eff}/molecule) vs. temperature are given in Fig. 4. At room temperature the magnetic moment for complex (**1**), $[Cr(\mu\text{-}OH)(BNIM)(HBNO)]_2$, is 8.12 B.M. If the complex had two Cr(III) metal ions as the only source for the measured magnetic moment,



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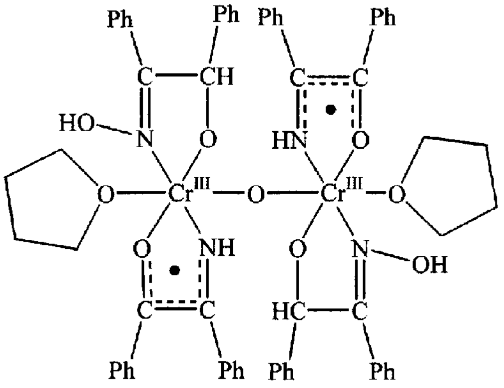

(2)

Figure 2. Suggested structures of $[Cr(III)(OH)(BNIM)(HBNO)]_2$ (**1**) and $[Cr(III)(BNIM)(HBNO)THF)]_2O$ (**2**) complexes.

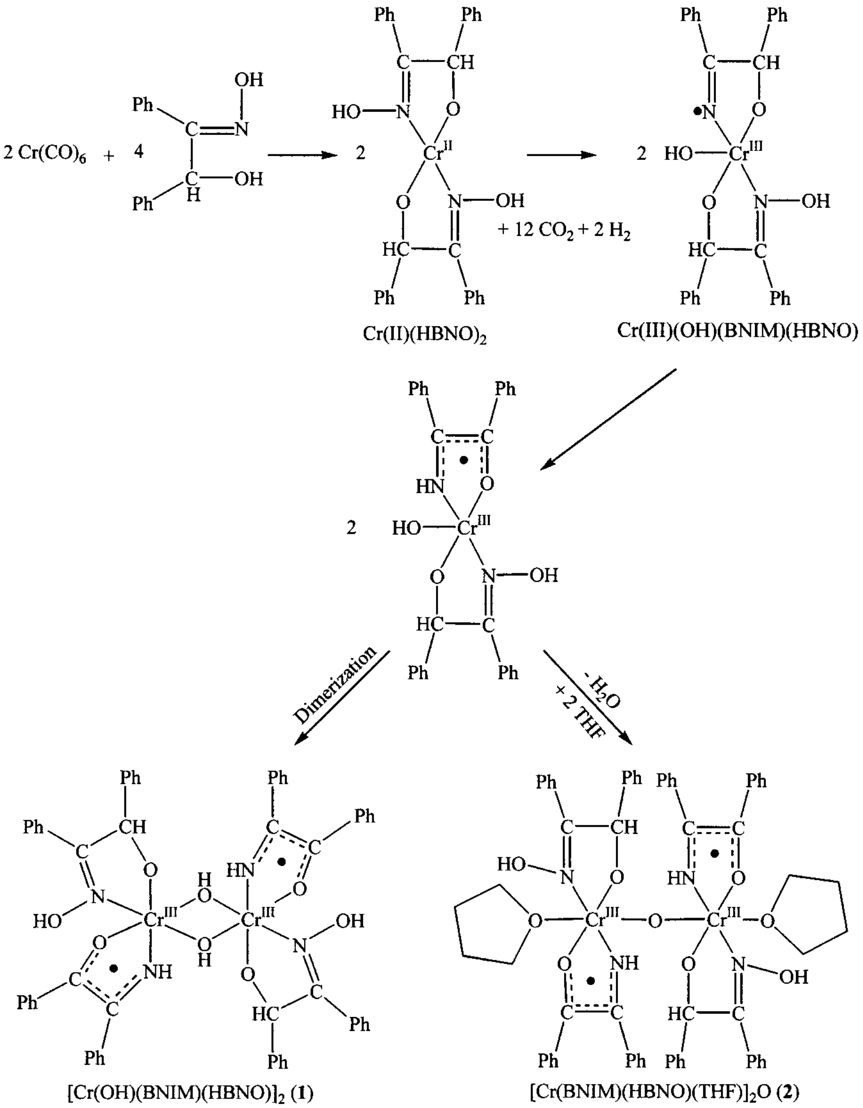

Figure 3. Suggested mechanism for the formation of [Cr(OH)(BNIM)(HBNO)]$_2$ (**1**) and [Cr(BNIM)(HBNO)(THF)]$_2$O (**2**) complexes.

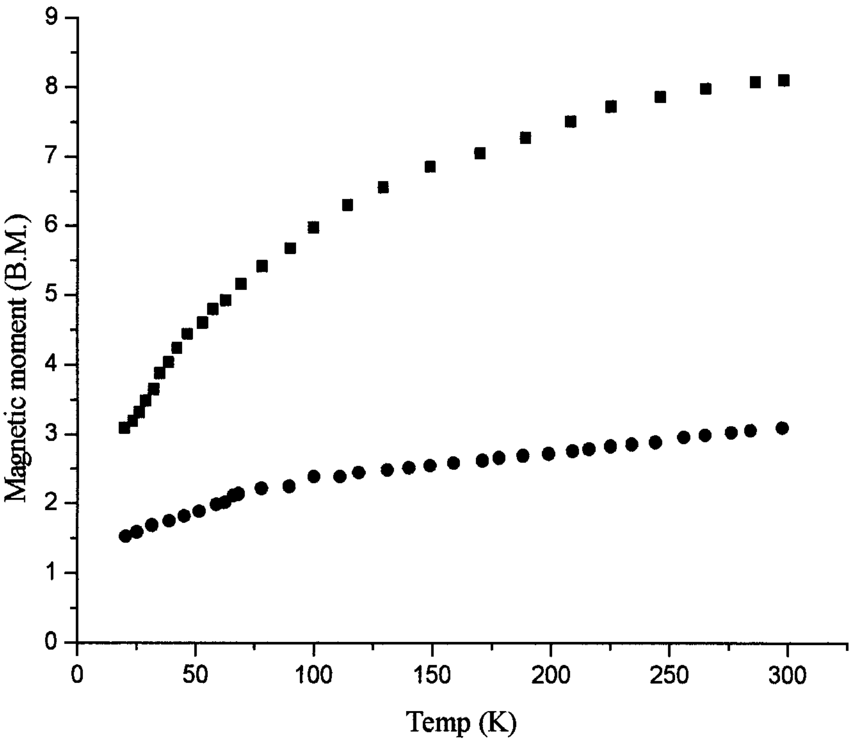

Figure 4. Plots of effective magnetic moments per molecules for solid samples of $[Cr(OH)(BNIM)(HBNO)]_2$ (**1**) (■) and $[Cr(BNIM)(HBNO)(THF)]_2O$ (**2**) (●) complexes as a function of temperature.

spin interactions between the two Cr(III) centers ($S_{cr} = 3/2$) would result in $S = 0$ as a ground-spin state and $S = 1$, 2 and 3 excited-spin states[37]. It would be expected for such dimer to have a maximum magnetic moment of 6.93 μ_B. However, the high μ_{eff} value observed for complex (**1**) may be explained if one views this compound in terms of two chromium(III), $S_{Cr} = 3/2$, metal ions interacting with two benzoin imine (BNIM), $S = 1/2$, radicals. An $S = 0$ ground state and $S = 1$, 2, 3 and 4 excited states would be expected. In case of a negligible exchange interaction, there would be thermal population of these excited states, and the spin-only value of μ_{eff}/molecule would be 8.94 B.M., whereas, a strong exchange interaction would lead to a thermal population in the ground state $S = 0$. Now it is obvious that the magnetic moment for complex (**1**) shows a very weak interaction behavior, which is temperature dependent, with the magnetic moment per dimer dropping from a value of 8.12 B.M. at 298K to 3.09 B.M. at 20K. The decrease of the effective magnetic moment with temperature was observed for the [Fe(DBSQ)(DBCAT)(dmbpy)] complex[38]. This compound showed a weak antiferromagnetic coupling between Fe(III) metal ion ($S = 5/2$) and the semiquinone ligand ($S = 1/2$). In contrast, complex (**2**) shows strong intramolecular exchange interactions that include Cr(III)-BNIM as well as Cr(III)-Cr(III) coupling through the bridging oxygen. A magnetic moment per dimer of 3.10 B.M. at 297.5K was observed which slightly drops to 1.53 B.M. at 20.5K. It is evident that the discrepancy of the magnetic behavior of the two dimers is attributed to the difference in bridging ligands connecting the two chromium metals[8,39,40]. In addition, mono-oxo-bridged metal ion dimers exhibit a shorter M-O-M bond distances and a greater degree of linearity, therefore, they exhibit a greater degree of exchange[39]. Such magnetic behavior compares very well with that reported[41,32,30] for $[Cr(phen)_2OH]_2^{4+}$, $[Fe(\mu\text{-OMe})(3,6\text{-DBSQ})_2]_2$, and $[Fe(salen)_2]_2O$. Unfortunately, the EPR spectra for the two chromium dimers in the solid state at room temperature are relatively uninformative. Broadened spectra were obtained with no hyperfine coupling resolved. The isotropic g values (g_{iso}) for complexes (**1**) and (**2**) were found to be 1.969 and 1.954, respectively, with a peak-to-peak width of ~230 G.

The effective magnetic moment per molecule (μ_{eff}/molecule) recorded at room temperature for the tris-complex, $Cr(HBNO)_3$, is 3.64 B.M. This value is quite close to the spin-only value of a d^3 metal ion ($S = 3/2$)[42] and fits best to the formulation of a complex containing chromium metal ion in the 3+ oxidation state.

Thermal Analysis

Thermal analysis (TGA) carried out on a solid sample of complex (**2**) at a heating rate of 10 °C/min. over a temperature range from room temperature to 800 °C is characterized by four decomposition steps (Table II). The first step commences at 73 °C, showing a slow decomposition up to 150 °C. In this stage the complex mainly loses one of the THF molecules (Table IV). This is followed by an abrupt loss in weight up to 350 °C with the elimination of the second THF molecule, a BNIM ligand, and a phenyl group of the other BNIM ligand. In the third stage, which covers a temperature range of 350–533 °C, decomposition of the remaining BNIM ligand takes place, in addition to the elimination of a phenyl group from the HBNO ligand. The fourth stage covers the temperature range of 533–750 °C with the elimination of a CO molecule.

Table II. Percentage Weight Losses and Corresponding Detached Species Encountered Upon Heating of the $[Cr(BNIM)(HBNO)(THF)]_2O$ (**2**) Complex

Step	Temp. (°C)	Fragment	Mol. Wt	Species decomposed	%Weight Loss	
					Calc.	Found
First	150	$C_{60}H_{52}N_4O_8Cr_2$	1061.05	THF 2H	6.35	6.24
Second	350	$C_{36}H_{24}N_3O_4Cr_2$	666.58	THF BNIM 2 OH, 2 H C_6H_5	37.18	37.56
Third	533	$C_{22}H_{14}N_2O_3Cr_2$	458.35	2 $C_6H_5O\text{-}C\text{-}C{=}N$	31.23	30.93
Fourth	750	$C_{21}H_{14}N_2O_2Cr_2$	430.34	CO	6.10	5.75

Table III. The Electronic Absorption Data for α-Benzoin Oxime and Its Chromium Complexes Recorded in DMF

Compound	λ, nm (ε, $M^{-1}\,cm^{-1}$)
H_2BNO	324 (11090), 370[a] (6073)
$Cr(HBNO)_3$	313 (13200), 558 (2547)
$[Cr(BNIM)(HBNO)(THF)]_2O$	310 (18452), 573 (2656), 992 (542)
$[Cr(\mu\text{-}OH)(BNIM)(HBNO)]_2$	319 (12041), 568 (2493)

[a] Shoulder.

Table IV. UV-Vis Spectroscopic Data of the Investigated Complexes

Complex	UV-Vis λ_{max} (ε $L\,mol^{-1}\,cm^{-1}$)[a]		
(**1**) $[Re(TTA)(H_2O)_4]Cl_2$	212 (250)	264 (510)	336 (510)
(**2**) $[Re(TTA)_2(H_2O)_2]Cl$	212 (410)	265 (820)	335 (800)
(**3**) $[ReO(TTA)(H_2O)_2]Cl_2$	212 (410)	260 (810)	336 (950)
(**4**) $[ReO(TTA)_2]Cl$	213 (380)	267 (720)	33 (950)
(**5**) $[In(TTA)(H_2O)_4]SO_4$	264 (710)	336 (950)	
(**6**) $[In(TTA)(HOTCA)_2]$	205 (320)	225 (700)	340 (300)
(**7**) $[In(TTA)(HTZT)_2]$	202 (470)	263 (350)	337 (220)
(**8**) [ReO(TTA)(HOTCA)[Cl	203 (390)	263 (710)	330 (900)

[a] ε are in the range of 10^2—10^3 for six-coordinate complexes of low symmetry (spin-allowed, Laporte-forbidden).

Electronic Spectra

Electronic absorption spectra recorded for the three chromium complexes in DMF solution over the range of 190–1100 nm are summarized in Table III. The resemblance of the spectra of the three complexes in the 190–800 nm range reinforces the similarity in charge distribution for these complexes. The UV-Vis region is characterized by two absorptions displayed by all three complexes. The intense absorption at the shorter wave length is assigned to a π-π* transition[4,43,44], while the absorption at the

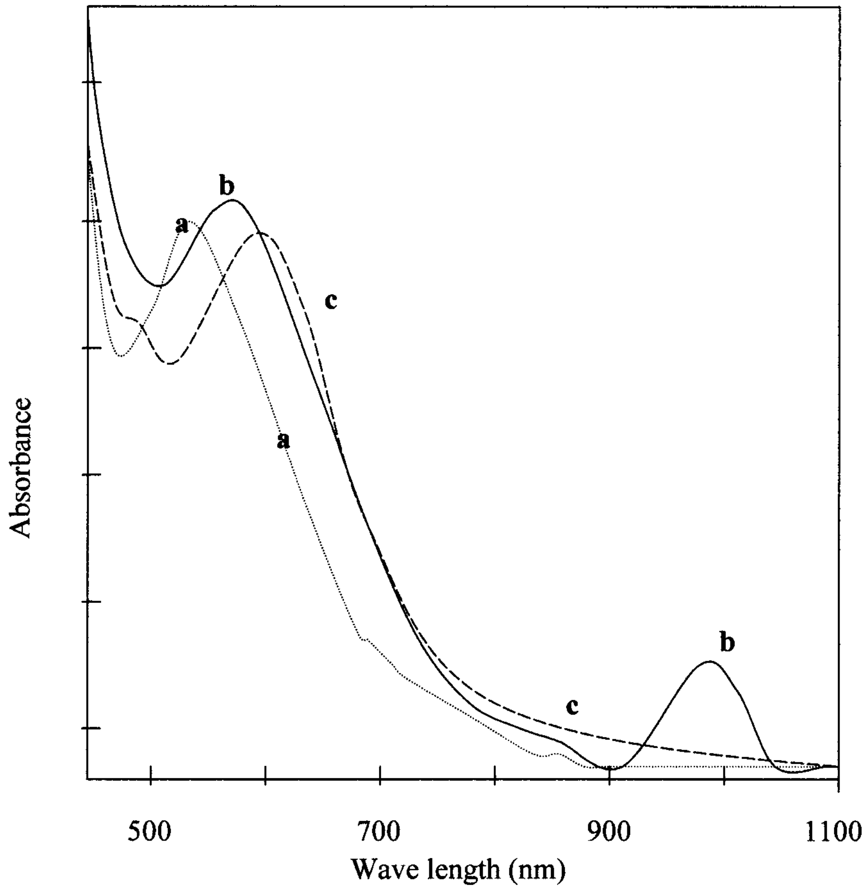

Figure 5. Electronic absorption spectra of $Cr(HBNO)_3$ (a), $[Cr(BNIM)(HBNO)(THF)_2O$ (b) and $[Cr(\mu\text{-}OH)(BNIM)(HBNO)]_2$ (c) in DMF solution.

longer wave length could be due to a chromium(III) $^4A_2 \rightarrow {}^4T_2$ transition[45], and/or n-π^* transition, which commonly displays a bathochromic shift upon complexation[4]. The other higher-energy d-d transitions characteristic for Cr(III) centers are obscured by the intense π-π^* transition and this is usually the case for complexes when the ligand associated with the metal contains aromatic rings[46]. The dominant feature of the electronic absorption spectrum for the $[Cr(BNIM)(HBNO)(THF)]_2O$ (**2**) complex, shown in Fig. 5, is a broad, low-energy band at 992 nm ($\varepsilon = 542\,M^{-1}\,cm^{-1}$). This band is most likely assignable to charge transfer associated with the central chromium metal ion and the chelate rings of the coordinated benzoin imines. Surprisingly, this ligand-to-metal charge transfer transition is not observed for the $[Cr(OH)(BNIM)(HBNO)]_2$ (**1**) complex. This may be attributed to the instability of the complex in DMF solution since it decomposes within a few minutes. The low solubility or the decomposition in most of the solvents limits solution studies of these complexes.

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