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Preparation, Structure, and Physical Properties of Dimeric Copper(II) Hydroxamate Complexes, Cu_2L_2 [L = *i*-PrN(O)C(=O)$(CH_2)_n$C(=O)N(O)-*i*-Pr, n = 3–10][1]

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Copper complexes of a series of dihydroxamic acids have been prepared and structurally characterized. For the series of ligands, L, of general formula *i*-$C_3H_7N(O)C(=O)(CH_2)_nC(=O)N(O)$-*i*-$C_3H_7$ (n = 3–6, 8, 10), the cupric complexes Cu_2L_2 are dimeric for n = 5–10 and dissolve in a variety of polar organic solvents. The complexes for n = 3 and 4 may be polymeric in the solid state and are extremely insoluble. The structure of the n = 5 dimer is composed of two square-planar Cu(II) ions coordinated by a cis arrangement of hydroxamate ligands with Cu–O(NO) and Cu–O(CO) distances of 1.88 and 1.91 Å, respectively. The dimer is centrosymmetric with a Cu–Cu distance of 6.26 Å. For space group $P2_1/c$, a = 14.538 (2) Å, b = 10.454 (2) Å, c = 11.177 (2) Å, and β = 95.03 (1)°. For Z = 2, d_{measd} = 1.36 g cm^{-3} and d_{calcd} = 1.38 g cm^{-3}; for 2011 observations and 193 variables R = 0.039 and R_w = 0.047. The magnetic susceptibilities from 5 to 300 K show Curie behavior with essentially spin-only behavior (1.73 μ_B); the values observed for n = 3–10 ranged from 1.80 to 1.85 μ_B. The EPR spectra of the complex dimers were measured at 110 K in methanol and chloroform/toluene glasses. The spectra for all the complexes except for n = 5 show the same basic pattern with $g_{\parallel} \simeq 2.23$, $A_{\parallel}$ = 21 mK, and $g \simeq 2.05$. Hyperfine splitting of the spectra for the ^{63}Cu and ^{65}Cu isotopes is resolved for the n = 6 and n = 8 complexes.

Introduction

Among the siderophores (microbial iron chelating agents[2]) rhodotorulic acid is distinguished by being a dihydroxamic acid (as opposed to the more common hexadentate ligands found in the siderophores). We have recently prepared synthetic analogues of rhodotorulic acid (RA)[3-5] and have reported the microbial iron transport characteristics of these analogues compared to the native siderophore.[6] However, in the field of analytical chemistry hydroxamic acids have long had a role that is independent of their function as iron transport agents for microorganisms. These ligands have found widespread use as analytical reagents for a variety of metal ions.[7] Yet in spite of their extensive analytical applications, few detailed structural studies have been made of the metal complexes that are formed. X-ray crystallographic data are available for the simple hydroxamate complexes: tris(benzohydroxamato)iron(III) dihydrate,[8] tris(benzohydroxamato)-chromium(III),[9] tetrakis(*N*-isopropyl-3,3-dimethylbutanohydroxamato)thorium(IV),[10] tetrakis(*N*-phenylbenzohydroxamato)hafnium(IV),[11] and bis(glycinohydroxamato)nickel(II).[12]

This paper describes the preparation and physical characterization of the series of complexes Cu_2L_2, where L = *i*-$C_3H_7N(O)C(=O)(CH_2)_nC(=O)N(O)$-*i*-$C_3H_7^{2-}$ (n = 3–10). The crystal structure of one member of this series, dicupric bis(*N*-isopropylpimel-*o*-hydroxamate), is presented—the first Cu(II) hydroxamate complex to be structurally characterized—and an unusual dimer.

Copper(II) complexes of hydroxamic acids are in general extremely insoluble in water; as a result, a principal use is in the isolation and purification of hydroxamic acid ligands.[13] General properties (electronic, infrared, and EPR spectra and magnetic susceptibilities) of a few Cu(II) hydroxamate complexes have been reported in the literature.[14,15] The syntheses of several Cu(II) *N*-phenyl dihydroxamate complexes have also been reported[16-18] for n = 2–5 methylene units separating the hydroxamate functional groups. The complexes were reported as $H_2Cu_8L_9$ (n = 2), Cu(LH)OH (n = 3), and CuL (n = 4, 5) on the basis of elemental analyses; no further characterization was reported. The results reported here disagree with these formulations.

In order to provide detailed structural and physical characterization of metal hydroxamate complexes, we have studied the copper(II) complexes of the series of dihydroxamate ligands *i*-$C_3H_7N(O)C(=O)(CH_2)_nC(=O)N(O)$-*i*-$C_3H_7$ (n = 3–6, 8, 10).

Experimental Section

Infrared spectra were obtained as KBr pellets by using a Perkin-Elmer 597 spectrophotometer. Visible spectra were recorded by using a Hewlett-Packard 8450A UV/vis spectrophotometer. Melting points were taken in open capillaries with a Mel-temp apparatus and are uncorrected. Temperature-dependent magnetic susceptibility measurements were made with a SHE Model 805 variable-temperature susceptometer, as described elsewhere.[19] The EPR spectra for samples in methanol or 1/1 chloroform/toluene glasses in quartz tubes were obtained at X-band frequencies at 110 K and at room temperature by using a Varian E-3 spectrometer with a liquid nitrogen flowing cryostat for low-temperature measurements. Elemental analyses were performed by the Analytical Laboratory, University of California, Berkeley.

Preparation of Compounds. The cupric complexes of the dihydroxamate ligands with n = 3–6, 8, and 10 were prepared by reaction of cupric nitrate with a slight excess of dihydroxamic acid in methanol. The "pH" (measured with an electrode standardized with aqueous buffer solutions) was raised to ~7–8 with methanolic NaOH. After the solution was allowed to stand at room temperature, blue crystals deposited for the n = 5, 6, 8, and 10 complexes. The n = 3 and n = 4 complexes precipitated as green-blue powders. A typical synthesis follows.

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Table I. Crystallographic Summary for **1**

mol formula	$C_{27}H_{52}Cu_2N_4O_9$
space group	$P2_1/c$ (No. 14)
a, Å	14.538 (2)
b, Å	10.454 (2)
c, Å	11.177 (2)
β, deg	95.03 (1)
V, Å^3	1692.1 (8)
d_{measd}, g cm^{-3}	1.36[a]
d_{calcd}, g cm^{-3}	1.38
Z	2
p value	0.030
2θ range for cell constants, deg	17.7–19.1[b]
$F(000)$, electrons	744
F_w	703.79
check reflections: the intensity of three standards measured every 7200 s showed an isotropic decrease of ~17% during 64 h of X-ray exposure and a correction was applied	
2θ range for data collection, deg	3.0–52.0
total reflcns measd	3690
data cryst dimens, mm	0.19 × 0.28 × 0.19
data cryst faces	(001), (00$\bar{1}$), ($\bar{1}$10), (1$\bar{1}$0), (110), ($\bar{1}\bar{1}$0)
abs coeff,[c] μ(Mo Kα), cm^{-1}	13.12

[a] Flotation in a mixture of CCl_4/heptane. [b] A total of six sets of four reflections per set, which were related by Laue symmetry $2/m$. [c] Examination of reflections with $\chi = 90 \pm 10°$ at approximately regular intervals ($5° < \Delta 2\theta < 10°$) within the 2θ range of data collection by the ψ scan technique gave normalized transmission factors for the data crystal of 0.79–0.81, and an absorption correction was included during data processing.

To 0.481 g (1.52 mmol) of *N,N'*-dihydroxy-*N,N'*-diisopropyldecanediamide in 250 mL of methanol was added 3.75 mL of aqueous $Cu(NO_3)_2$ (0.397 M; 1.49 mmol) to afford a bright green solution. The "pH" (as measured by a glass electrode) was raised to 7.8, and the color changed from green to blue. Precipitation of the product was complete after ~10 min. The blue-gray microcrystals were washed with methanol to yield 0.55 g (0.65 mmol) of $Cu_2L_2{\cdot}CH_3OH$.

Cupric complexes of the other dihydroxamate ligands were prepared by the same procedure. For $n = 5$ and 6, the complexes precipitated more slowly and were left to stand between 12 and 72 h for complete precipitation of the product.

Dicupric bis(*N,N'*-dihydroxy-*N,N'*-diisopropyldodecanediamide): mp 199 °C dec; IR ν (cm^{-1}) 1570, 1576 (s, C=O); yield 96%. Anal. Calcd for $Cu_2(C_{18}H_{32}N_2O_4)_2{\cdot}CH_3OH$: C, 52.65; H, 8.60; N, 6.64; Cu, 15.7. Found: C, 52.36; H, 8.47; N, 6.76; Cu, 15.5.

$n = 8$. Dicupric bis(*N,N'*-dihydroxy-*N,N'*-diisopropyldecanediamide): mp 199 °C dec; IR ν (cm^{-1}) 1570, 1576 (s, C=O); yield 93%. Anal. Calcd for $Cu_2(C_{16}H_{34}N_2O_4)_2{\cdot}CH_3OH$: C, 50.30; H, 8.12; N, 7.11; Cu, 15.1. Found: C, 49.94; H, 8.05; N, 7.06; Cu, 15.9.

$n = 6$. Dicupric bis(*N,N'*-dihydroxy-*N,N'*-diisopropyloctanediamide): mp 237 °C dec; IR ν (cm^{-1}) 1570, 1576 (s, C=O); yield 90%. Anal. Calcd for $Cu_2(C_{14}H_{26}N_2O_4)_2{\cdot}CH_3OH$: C, 47.59; H, 8.19, N, 7.66; Cu, 17.4. Found: C, 47.49; H, 7.56; N, 7.66; Cu, 17.5.

$n = 5$. Dicupric bis(*N,N'*-dihydroxy-*N,N'*-diisopropylheptanediamide): mp 256 °C dec; IR ν (cm^{-1}) 1570, 1580 (s, C=O); yield 90%. Anal. Calcd for $Cu_2(C_{13}H_{24}N_2O_4)_2{\cdot}CH_3OH$: C, 46.09; H, 7.45; N, 7.96; Cu, 18.1. Found: C, 46.17; H, 7.36; N, 7.85; Cu, 17.8.

$n = 4$. Cupric *N,N'*-dihydroxy-*N,N'*-diisopropylhexanediamide: mp 267 °C (decomposes explosively); IR ν (cm^{-1}) 1570, 1578 (s, C=O); yield 95%. Anal. Calcd for $CuC_{12}H_{22}N_2O_4{\cdot}H_2O$: C, 42.41; H, 7.12; N, 8.24; Cu, 18.7. Found: C, 42.87; H, 6.94; N, 8.27; Cu, 18.2.

$n = 3$. Cupric *N,N'*-dihydroxy-*N,N'*-diisopropylpentanediamide: mp 270 °C (decomposes explosively); IR ν (cm^{-1}) 1570, 1578 (s, C=O); yield 96%. Anal. Calcd for $CuC_{11}H_{20}N_2O_4{\cdot}H_2O$: C, 40.54; H, 6.81; N, 8.60; Cu, 19.5. Found: C, 40.21; H, 6.22; N, 8.35; Cu, 19.1.

X-ray Crystallography. Single crystals of the Cu(II) $n = 5$ complex (**1**) formed from methanol solution at room temperature as dark blue parallelepipeds. Because the crystals lost solvent when exposed to the atmosphere, a well-formed crystal was wedged into a thin-walled capillary and examined by precession photography. This established the space group as $P2_1/c$. Preliminary study of intense, low-angle ($2\theta < 19°$) reflections from this crystal with an Enraf-Nonius CAD4 automated diffractometer confirmed this symmetry and indicated that the crystal had good mosaic character; the peak widths at half-height, as determined by ω scans with a receiving aperature of 1 mm, were 0.25–0.35 Å and thus were satisfactorily narrow. After accurate centering of 24 high-angle reflections chosen from diverse regions of reciprocal space, a unique set of intensity data was gathered as previously reported.[20] Crystal data and those variables of data collection that are relevant to this study are summarized in Table I.

Table II. Fractional Coordinates of Non-Hydrogen Atoms[a]

atom	x	y	z
Cu	0.21038 (3)	0.01450 (4)	0.08587 (4)
O(1)	0.3035 (2)	−0.1074 (3)	0.1246 (2)
O(2)	0.1506 (2)	−0.0663 (2)	0.2118 (2)
O(3)	0.2735 (2)	0.1006 (2)	−0.0310 (2)
O(4)	0.1155 (2)	0.1384 (2)	0.0467 (2)
N(1)	0.2794 (2)	−0.1805 (3)	0.2193 (3)
N(2)	0.2197 (2)	0.2006 (3)	−0.0760 (3)
C(1)	0.1996 (3)	−0.1565 (4)	0.2601 (3)
C(2)	0.1396 (3)	0.2170 (3)	−0.0323 (3)
C(3)	0.3498 (3)	−0.2728 (4)	0.2631 (4)
C(4)	0.3703 (4)	−0.3619 (4)	0.1635 (5)
C(5)	0.4353 (3)	−0.2012 (5)	0.3140 (5)
C(6)	0.2610 (3)	0.2779 (4)	−0.1661 (3)
C(7)	0.2860 (3)	0.1930 (5)	−0.2670 (4)
C(8)	0.3418 (3)	0.3512 (5)	−0.1099 (5)
C(9)	0.0747 (3)	0.3224 (4)	−0.0736 (4)
C(10)	0.0141 (3)	0.2900 (4)	−0.1869 (4)
C(11)	−0.0695 (3)	0.3758 (4)	−0.2041 (4)
C(13)	0.1627 (3)	−0.2325 (4)	0.3596 (4)
C(12)	0.1259 (3)	−0.3641 (4)	0.3250 (4)
O(5,1)	0.457 (1)	0.040 (2)	−0.068 (2)
O(5,2)	0.525 (1)	−0.012 (2)	−0.089 (2)
C(14)	0.504 (1)	0.024 (1)	−0.003 (2)

[a] See Figure 1 for identity of atoms. Numbers in parentheses are estimated standard deviations.

The structure was solved by standard heavy-atom procedures and refined by full-matrix least-squares methods,[20] using only reflections with $F_o^2 > 3\sigma(F_o^2)$. Neutral-atom scattering factors for Cu, O, N, C, and H, corrected for anomalous scattering of Mo Kα radiation,[20] were used in these calculations. The hydrogen atoms were located from a difference Fourier map (at densities of 0.3–0.5 e Å^{-3}) and were fixed at idealized positions[21] during the concluding cycles of refinement.[22] The methanol of crystallization is severely disordered about the inversion center at ($^1/_2$, 0, 0) and was refined by using a model with two alternate positions for the oxygen atoms and the carbon atom slightly displaced from the inversion center. The methyl hydrogens were not located. In the final cycle of refinement, in which all non-hydrogen atoms except those of the methanol molecule were treated anisotropically, no shift in a parameter was significant relative to its estimated standard deviation with final R = 0.039 and R_w = 0.047 and an error in an observation of unit weight of 1.88[23] for 2011 observations and 193 variables. The largest peaks in the final difference Fourier were 0.4–0.5 e Å^{-3} and were associated with the methanol oxygen and carbon atoms. Comparison of F_o vs. F_c as a function of F_o, setting angle, and Miller index showed minor disagreement only among the very weak reflections.

The positional parameters and esd's are given in Table II; anisotropic thermal parameters (Table III), hydrogen atom parameters (Table IV), observed and calculated structure factor amplitudes (Table V), and magnetic susceptibility data (Table VII) are available as supplementary material.[24]

Results and Discussion

The Cu(II) complexes with $n = 5$, 6, 8, and 10 are soluble in a wide range of solvents [including $CHCl_3$, CH_2Cl_2, DMF, pyridine, and alcohols (slightly)]. The X-ray structure of the $n = 5$ complex, described below, indicates that these complexes are dimeric. This is also supported by molecular weight measurements of the cupric complex of the rhodotorulate anion, which indicates that it also is dimeric.[25] Crystalline samples of the complexes

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(21) The C–H distances were constrained to 0.95 Å in accordance with a previous study: Churchill, M. R. *Inorg. Chem.* **1973**, *12*, 1213.

(22) Hydrogen atoms were assigned fixed thermal parameters of 5.0 Å^2 in least-squares refinement.

(23) The function minimized in refinement is $\sum w(F_o - F_c)^2$, where the weight w is $4F_o^2/\sigma(F_o^2)$. The error indices R, R_w, and the standard deviation in an observation of unit weight are defined in ref 20.

(24) See paragraph at end of paper regarding supplementary material.

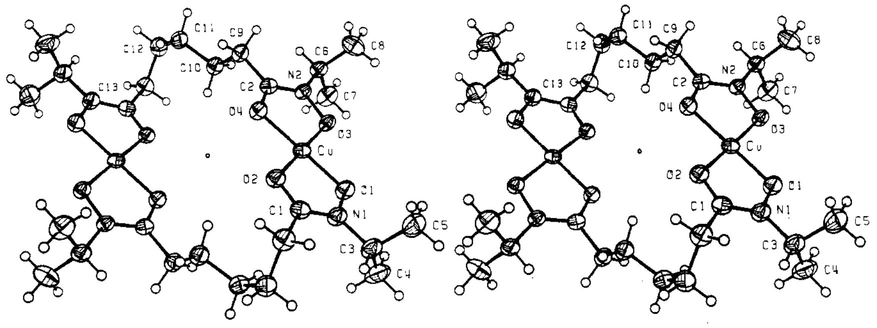

Figure 1. Stereoscopic view of the structure of Cu_2L_2 (n = 5) (**1**) illustrating the numbering scheme used herein. Atoms are drawn as ellipsoids of 30% probability; hydrogen atoms are shown as spheres of radius 0.1 Å.

for n = 5 and 10 were obtained; however, only for the n = 5 ligand were crystals large enough for X-ray diffraction studies. The copper(II) complexes for n = 3 and 4 are obtained as powders, and different batches range in color from very light green to blue-gray. Elemental analyses and infrared spectra are independent of the color of the complex isolated. The powders are extremely insoluble in all solvents except pyridine, in which they are only sparingly soluble. This suggests that the n = 3 and 4 complexes are highly associated in the solid state.

X-ray Crystallography. Figure 1 is a stereoscopic view of the crystal structure of the n = 5 complex (**1**). Selected interatomic distances and angles are presented in Table VI.

As shown in Figure 1, **1** is dimeric and possesses crystallographic C_i symmetry. The two tetradentate hydroxamate ligands bridge the two Cu(II) ions with the coordination geometry being square planar and ligands cis. The Cu···Cu′ distance is 6.256 (1) Å. The two methanolic oxygen positions are within normal hydrogen-bonding distances [2.807 (29) and 2.848 (20) Å] from the N-hydroxy oxygens of the hydroxamate ligands [O(3) and O(1)]. There is no association of molecules to give additional ligation to the copper; the closest intermolecular contacts to the copper atom are greater than 3.8 Å. The copper coordination site is therefore square planar, with only coordination from the oxygen atoms of the hydroxamate ligand. The ligands are planar, with a maximum deviation from the plane of 0.06 Å. A packing diagram is presented in the supplementary material.[24]

Magnetic Susceptibility Measurements. Temperature-dependent magnetic susceptibility measurements of the complexes $Cu_2L_2 \cdot CH_3OH$ for chain lengths 3, 5, and 10 show that they exhibit Curie behavior over the temperature range 5–300 K. Table VII[24] lists the susceptibilities (per Cu^{2+}, corrected for diamagnetic contributions and temperature-independent paramagnetism) measured as a function of temperature. Magnetic moments calculated from plots of inverse molar susceptibility ($1/\chi'$) vs. temperature (obtained by fitting the data with a general linear least-squares program): n = 3, 1.80 μ_B; n = 5, 1.80 μ_B; n = 10, 1.85 μ_B. These values are consistent with the values of 1.78–1.99 μ_B calculated for other copper hydroxamate complexes.[14,16–18] Since the spin-only value expected for one unpaired electron is 1.73 μ_B, the magnetic behavior of these dimeric complexes indicates the absence of any strong magnetic interactions between the copper ions.

Electronic Spectra. The visible spectra of the copper dihydroxamate complexes in methanol solution consist of two bands at 350 nm (ϵ ~150 M^{-1} cm^{-1} per Cu^{2+}) and 620 nm (ϵ ~25 M^{-1} cm^{-1} per Cu^{2+}). The band at 620 nm is broad and extends from about 500 to 800 nm. These results are in agreement with those reported for the simple monomeric complex $Cu[CH_3C(=O)N(O)CH_3]_2$[14] in ethanol (λ_{max} 345, 629 nm) and those reported recently for monomeric Cu(II) thiohydroxamate complexes [λ_{max} 550 nm (ϵ ~300 M^{-1} cm^{-1}) and 830 nm (ϵ ~20 M^{-1} cm^{-1})].[26] In the latter complexes, both of the transitions were assigned as being d–d in character, with the weak band at 820 nm assigned as the $z^2 \rightarrow x^2 - y^2$ transition. No mention was made of the nature of the band at 345 nm for $Cu[CH_3C(=O)N(O)CH_3]_2$,[14] nor were any extinction coefficients given.

Table VI. Bond Lengths (Å) and Bond Angles (deg) for **1**[a]

Cu–O(1)	1.881 (2)	N(1)–C(3)	1.459 (4)
Cu–O(3)	1.889 (2)	N(2)–C(6)	1.460 (3)
mean[b]	1.885 (4)	mean	1.460 (2)
Cu–O(2)	1.914 (2)	C(3)–C(4)	1.501 (5)
Cu–O(4)	1.915 (2)	C(3)–C(5)	1.519 (5)
mean	1.915 (4)	C(6)–C(7)	1.504 (4)
Cu···Cu	6.256 (1)	C(6)–C(8)	1.493 (5)
O(1)–N(1)	1.375 (3)	C(9)–C(10)	1.516 (4)
O(3)–N(2)	1.375 (3)	C(10)–C(11)	1.511 (4)
mean	1.375 (2)	C(11)–C(12)	1.523 (5)
		C(12)–C(13)	1.514 (5)
O(2)–C(1)	1.273 (3)	O(5,1)–O(3)	2.807 (19)[c]
O(4)–C(2)	1.277 (3)	O(5,2)–O(1)	2.848 (2)
mean	1.275 (2)		

O(1)–Cu–O(2)	84.02 (8)	N(1)–C(1)–C(13)	122.8 (3)
O(1)–Cu–O(3)	95.64 (8)	N(2)–C(2)–C(9)	122.5 (3)
O(1)–Cu–O(4)	179.90 (8)	mean	122.7 (2)
O(2)–Cu–O(3)	176.42 (8)	O(1)–N(1)–C(3)	114.1 (2)
O(2)–Cu–O(4)	95.88 (8)	O(3)–N(2)–C(6)	114.8 (2)
O(3)–Cu–O(4)	84.46 (8)	mean	114.5 (4)
O(1)–N(1)–C(1)	117.0 (2)		
O(3)–N(2)–C(2)	117.2 (2)	C(1)–N(1)–C(3)	128.8 (3)
mean	117.1 (1)	C(2)–N(2)–C(6)	128.0 (2)
O(2)–C(1)–C(13)	118.9 (3)	mean	128.4 (4)
O(4)–C(2)–C(9)	118.9 (3)		
mean	118.9 (2)		

[a] Numbers in parentheses are the estimated standard deviations in the least significant digits. See Figure 1 for the identity of the atoms. [b] Averages are computed as $\bar{x} = 1/n\sum x_i$ and the standard deviations in the means are computed from the larger of the variance, $\sigma^2(\bar{x}) = \sum(x - \bar{x})^2/[n(n-1)]$ or the average standard deviation: $1/\sigma^2(\bar{x}) = \sum 1/\sigma^2(x_i)$. [c] O(5,1) and O(5,2) are the disordered oxygens of the methanol molecule.

The visible spectra of the bis(hydroxamato)copper(II) complexes are similar to those of Cu(II) β-diketonates.[27–31] There has been much discussion in the literature concerning the electronic ground state of $Cu(acac)_2$. Much of the controversy concerned the nature of a band at 385 nm; i.e., is it d–d or charge transfer in nature? The polarized electronic absorption spectrum of bis(dipivaloylmethanido)copper(II)[29] provides strong evidence for four overlapping bands at about 500, 550, 610, and 640 nm due to four d–d transitions (d_{yz}, $d_{x^2-y^2}$, d_{xz}, and $d_{z^2} \rightarrow d_{xy}$). This is in agreement with LCAO–MO calculations[30] which predict that the d_{xy} orbital lies ~20 000 cm^{-1} higher in energy than the other four d orbitals, all of which lie relatively close together. This predicts that all four d–d transitions occur in the region 500–650 nm, and

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thus the band at 385 nm was assigned as a spin-forbidden ligand-based charge-transfer band. On the basis of these observations, which have also been found to apply to various Cu(II) bis(salicylaldiminato) complexes,[31] the near-UV absorbance at 350 nm in the Cu(II) dihydroxamate complexes probably is also charge transfer in nature. The aluminum dihydroxamate complexes, Al_2L_3, also exhibit a weak band in the near-UV region [λ_{max} 302 nm (sh) (ϵ ~20 M^{-1} cm^{-1})], which suggests that the charge-transfer band in the spectra of the copper complexes is ligand-based.

The visible spectrum in the region 470–800 nm was measured in several solvents for the $n = 8$ complex and was found to be slightly solvent dependent. In chloroform and dichloromethane, $\lambda_{max} = 616$ nm (ϵ ~19 M^{-1} cm^{-1}), and in DMF, $\lambda_{max} = 616$ nm (ϵ ~20 M^{-1} cm^{-1}). In both solvents, there is also a shoulder at ~540 nm, which is at a slightly higher wavelength in DMF. In pyridine, $\lambda_{max} = 620$ (ϵ ~23 M^{-1} cm^{-1}) with a shoulder at ~570 nm. Due to the overlapping of the d–d transitions, very little can be said concerning the actual assignment of the bands. The invariance of λ_{max} with changes in solvent basicity suggest that the $d_{x^2-y^2} \rightarrow d_{xy}$ transition occurs at ~620 nm, giving a value of $10D_q$ of ~16 000 cm^{-1} [compared with 18 000 cm^{-1} for $Cu(acac)_2$, 17 000 cm^{-1} for $Cu(Me\text{-}Sal)_2$, and 16 800 cm^{-1} for $Cu(Pr\text{-}Sal)_2$].[31] On the basis of the energy level calculations for $Cu(acac)_2$, the shoulder that is observed at 540 and 570 nm is probably the $d_{yz} \rightarrow d_{xy}$ transition. The red shift of this band with increasing solvent basicity is consistent with axial coordination by donor solvents.

The visible spectrum was measured as a function of pH in methanol solution for $n = 3$–8. Although the complexes with $n = 3$ and 4 precipitate slowly at or above neutral pH, even at millimolar concentrations, the precipitation process was slow enough that no precipitation occurred during the titration. Figure 2 shows the visible spectrum as a function of pH for the $n = 3$ ligand with a Cu/L ratio of 1/1 (spectrophotometric titrations with the other dihydroxamate ligands yield similar spectra). Isosbestic points occur at 300, 426, 496, and 632 nm in Figure 2. As the pH is lowered, the solution changes color from blue to green due to the protonation of the bis(hydroxamate) complex and formation of mono(hydroxamate) species. Protonation of the dimeric complexes may take place in one- or two-proton steps:

$$Cu_2L_2 + H^+ = Cu_2LLH^+ \tag{1}$$

$$Cu_2LLH^+ + H^+ = Cu_2L^{2+} + LH_2 \quad (\text{or } 2CuLH^+) \tag{2}$$

$$Cu_2L_2 + 2H^+ = Cu_2L^{2+} + LH_2 \tag{3}$$

$$Cu_2L_2 + 2H^+ = 2CuLH^+ \tag{4}$$

Using the method of Schwarzenbach,[32] one may derive the following relationships for these reactions:

$$A_{obsd} = K_H(A_0 - A_{obsd})/[H^+] + \epsilon_2 c_T \tag{5}$$

$$A_{obsd} = 2K_H(A_0 - A_{obsd})[LH_2]/[H^+]^2 + \epsilon_2 c_T \tag{6}$$

$$A_{obsd} = 2K_H(A_0 - A_{obsd})[CuLH]/[H^+]^2 + \epsilon_2 c_T \tag{7}$$

where A_0 is the initial absorbance, A_{obsd} is the absorbance at any point during the titration, K_H is the protonation constant defined by reactions 1–4, and c_T is the total concentration of copper-containing species in the solution. Only for reaction 1 will a plot of A_{obsd} vs. $(A_0 - A_{obsd})/[H^+]$ be a straight line. This is true if either (a) the protonations are widely separated in pH (unlikely here) or (b) the absorbance spectra of the mono- or bis(hydroxamato)copper(II) complexes are independent of whether they are monomers or dimers (quite likely). For reaction 3 or 4 the varying concentration of the product species (LH_2 or $CuLH^+$, respectively) generates a nonlinear relationship that will not give a simple relationship of A_{obsd} vs. pH. Figure 3 shows a Schwarzenbach plot modeling reaction 1 for the $n = 5$ complex. Plots with the other ligands are also linear. This suggests that protonation of the dimeric complexes occurs in two successive, one-proton steps.

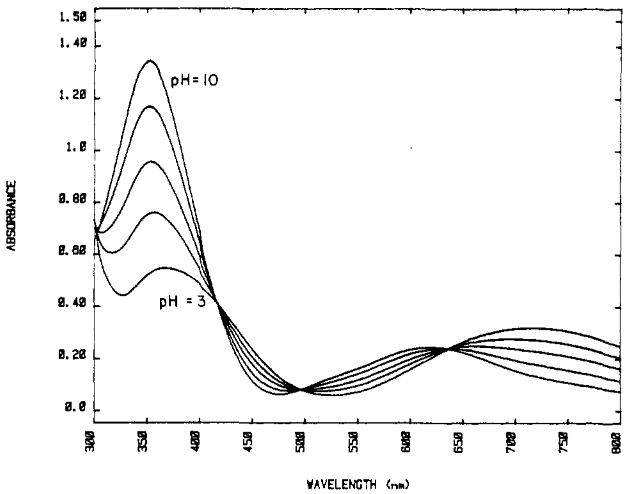

Figure 2. Spectrophotometric titration of the Cu(II) $n = 3$ complex in methanol. $[Cu^{2+}]_T = 5.18$ mM; Cu/L = 1/1.

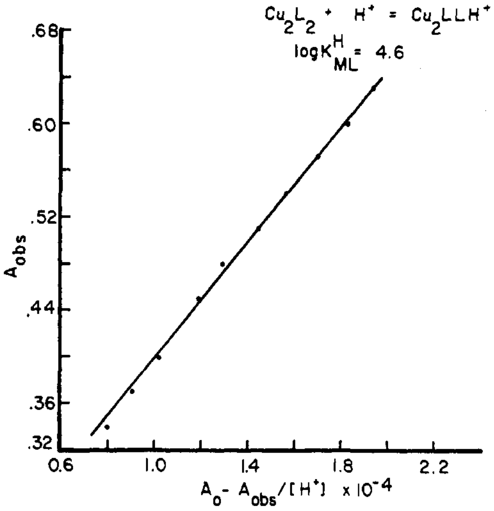

Figure 3. Schwarzenbach plot for the first protonation reaction of Cu_2L_2 ($n = 5$) in 10% aqueous methanol with $[Cu]_T = 10$ mM; Cu/L = 1/1.

The fully protonated mono(hydroxamate) complexes may be either monomeric or dimeric, depending on the ratio of metal to ligand:

$$CuLH^+ + Cu^{2+} = CuLCu^{2+} + H^+ \tag{8}$$

$$CuLCu^{2+} + LH_2 = 2CuLH^+ \tag{9}$$

Electron Paramagnetic Resonance. The EPR spectra of the copper dihydroxamate complexes were measured at 110 K in methanol and chloroform/toluene glasses and are shown in Figures 4 and 5, respectively. Relatively narrow lines were obtained for spectra measured in chloroform/toluene glasses, whereas spectra of the methanol glasses are broad and not as well resolved. It has been observed[33] that the degree of spectral resolution in various Cu(II) systems is highly dependent upon the nature of the solvent forming the glass matrix, with $CHCl_3$/toluene mixtures often giving well-resolved spectra. The spectra of all the complexes (except for $n = 5$) have the same basic pattern (Figures 4 and 5) with spin-Hamiltonian parameters[34] ($g_\parallel \simeq 2.23$; $A_\parallel = 21.0$ mK;

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[32] Schwarzenbach, G.; Schwarzenbach, K. *Helv. Chim. Acta* **1963**, *46*, 1390.

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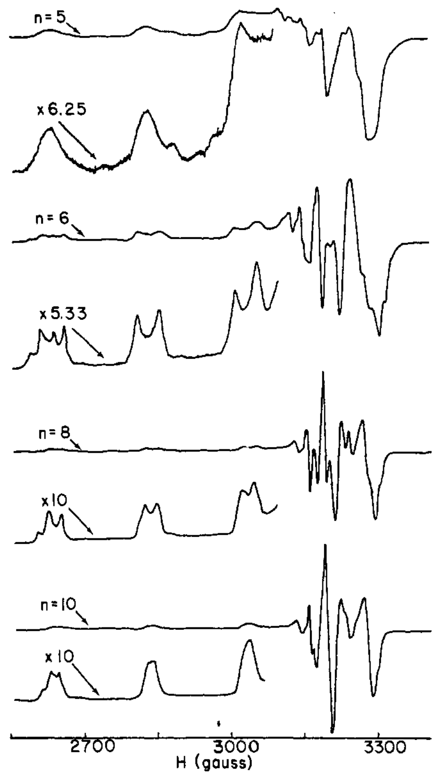

Figure 4. EPR spectra of Cu_2L_2 complexes at X-band frequency (ν = 9.140 GHz) in methanol glass at 110 K.

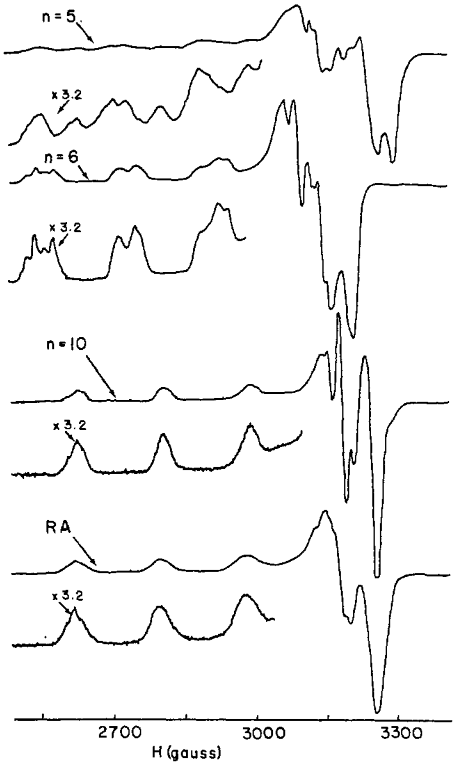

Figure 5. EPR spectra of Cu_2L_2 complexes at X-band frequency (ν = 9.140 GHz) in chloroform/toluene (1/1) glass at 110 K. RA = rhodotorulic acid; other ligands, as described in text.

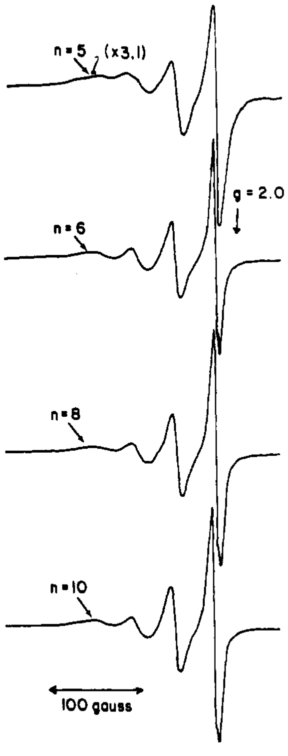

Figure 6. EPR spectra of Cu_2L_2 complexes at X-band frequency (ν = 9.135 GHz) at room temperature in $CHCl_3$/toluene (1/1) solution.

$g_\perp \sim 2.031$) that are similar to those of Cu(acac)$_2$.[35]

The EPR spectra for the $n = 6$ and $n = 8$ complexes are well resolved, and the $M_I = -^3/_2$ (low-field) features appear to consist of the superposition of three or four peaks. Examination of the $g_\perp$ region of the $n = 10$ spectrum reveals evidence of similar splittings that are less well resolved. The splitting of the $M_I = -^3/_2$ line into four components for the $n = 6$ complex indicates that the solution contains two major chemical components, each with well-resolved features due to ^{63}Cu and ^{65}Cu isotopes (^{63}Cu, 69%; ^{65}Cu, 31%; $I = ^3/_2$). The $g_\perp$ values for the two components are $g_\parallel \sim 2.25$ ($A_\parallel$ = 21.3 mK) and 2.22 ($A_\parallel$ = 21.0 mK). In the other complexes, the $M_I = -^3/_2$ lines due to the two components may overlap and appear as three lines instead of four. The isotopic splitting of the $M_I = -^1/_2$ and $+^1/_2$ lines is not resolved; however, two lines due to the two chemical components are visible. Similar splitting of the $M_I = -^3/_2$ (and $-^1/_2$) lines was observed for the Cu(II) thiohydroxamate complexes in frozen DMF and acetonitrile, but not in $CHCl_3$/toluene.[26] Becher et al.[26] propose that this could be caused by solvation of some of the copper chelate molecules in the axial position by DMF or acetonitrile. However, they observed no band shifts in the electronic spectra in donor solvents such as DMF or pyridine, indicating that any axial ligation by donor molecules must be very weak.

Since two chemical components are observed here both in frozen methanol (Figure 4) and $CHCl_3$/toluene, it would appear that solvation of some of the molecules in the axial position as an explanation for the observed line splittings is unlikely. The crystalline compounds from which the EPR solutions were prepared contain half of a molecule of methanol per copper atom; therefore, there is a small amount of methanol present in the chloroform solutions. That there is no association of the methanol molecule with the copper ion in the solid state suggests that it is unlikely that the methanol interacts strongly with the copper ion when diluted to millimolar concentrations with chloroform/toluene; that the ratio of the two components does not change significantly when pure methanol is used as the solvent also argues against methanol solvation of the complex in $CHCl_3$/toluene. A more likely explanation is the presence of significant quantities of two geometric isomers in solution. Molecular models indicate that, for n = 6–10, all possible combinations of cis–trans isomers may be formed; the cis–cis and trans–trans isomers (which have inversion symmetry) appear to be sterically the most favorable.

The EPR spectrum of the $n = 5$ complex is broad and much less resolved than the other complexes and exhibits additional features. The differences probably are due to a weak dipolar

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[35] Gersmann, H. R.; Swalen, J. D. *J. Chem. Phys.* **1962**, *36*, 3221.

interaction between the two Cu^{2+} ions analogous to that observed in the EPR spectra of the ferric dihydroxamate complexes.[5]

The room-temperature solution EPR spectra of the complexes were also measured in $CHCl_3$/toluene (1/1) and are shown in Figure 6. The spectra are all superimposable (except that the spectrum of the $n = 5$ complex is reduced in intensity) with $g_{\parallel} \sim 2.11$ and $A_{\parallel} \sim 7.9$ mK. The $M_I = {}^3/_2$ line still shows evidence of some splitting for $n = 6$–10, indicating that the two components can be differentiated even at room temperature, although their spectra are almost superimposable.

In conclusion, the Cu(II) complexes of the series of dihydroxamate ligands $i\text{-}C_3H_7N(O)C({=}O)(CH_2)_nC({=}O)N(O)\text{-}i\text{-}C_3H_7^{2-}$ have been prepared and characterized. For $n = 3$ and 4 the complexes appear to be polymeric. For $n \geq 5$ the complexes are dimeric and appear to exist as two principal geometric isomers in solution.

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Registry No. 1, 103693-86-3; Cu_2L_2 ($n = 4$), 103693-90-9; Cu_2L_2 ($n = 6$), 103693-89-6; Cu_2L_2 ($n = 3$), 103693-91-0; Cu_2L_2 ($n = 8$), 103693-88-5; Cu_2L_2 ($n = 10$), 103693-87-4.

Supplementary Material Available: Table III (anisotropic thermal parameters of non-hydrogen atoms), Table IV (fractional coordinates of hydrogen atoms), Table VII (temperature-dependent magnetic susceptibility data for the complexes Cu_2L_2), and a packing diagram of the Cu_2L_2 dimer for $n = 5$ (4 pages); Table V (structure factor amplitudes) (13 pages). Ordering information is given on any current masthead page.

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Optical Spectroscopy as a Structural and Electronic Probe in a Coordination Compound: $[(NH_3)_5CrOHCr(NH_3)_5]Cl_5{\cdot}H_2O$

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Single crystals of $[(NH_3)_5CrOHCr(NH_3)_5]Cl_5{\cdot}H_2O$ were studied by absorption, Zeeman, and site-selective luminescence spectroscopy in the temperature range 1.5–95 K. The existence of two nonequivalent dimer sites was established, and their orientations in the crystal were determined. Exchange splittings, zero-field splittings, and excited-state *g* values were determined separately for each site. Nonradiative transfer of excitation energy between inequivalent sites was observed at temperatures above 15 K.

Introduction

Structural and electronic properties of transition-metal complexes are often derived from measurements of their bulk properties in the solid state. X-ray diffraction is the most widely used and, in general, the most powerful technique for obtaining molecular structure information. Measurements of the magnetic susceptibility and, less commonly, the heat capacity are used to derive information about low-lying electronic states. They are particularly useful in spin-crossover situations[1] and for the study of exchange-coupled systems.[2] Bulk techniques require the existence of a reasonable molecular model, which can be fitted to the experimental data. They provide an average picture but no direct access to the molecular properties. In cases of structural disorder, subtle superstructures, or very large unit cells the potential of X-ray diffraction may be greatly reduced. This is particularly true for the elucidation of coordination geometries of active metallic sites in metalloproteins. In this currently very active field of research, spectroscopic techniques play a dominant part in obtaining structural information.[3]

We have chosen a classical coordination compound, the acid rhodo chromium(III) complex, to demonstrate the power of optical spectroscopic techniques for the elucidation of structural and electronic properties. There exist two distinct modifications of acid rhodo chromium (III) chloride, a monohydrate and a dihydrate.[4] Both of these have been structurally characterized. The present study is concerned with the monohydrate, the dihydrate being only used as a reference. There are two conflicting reports of the crystal structure of $[(NH_3)_5CrOHCr(NH_3)_5]Cl_5{\cdot}H_2O$, both based on single-crystal X-ray diffraction measurements. Urushiyama et al.[5] published a very brief note in which they assigned the space group to $P4_12_12$ (or $P4_32_12$) with $a = 16.26$ Å, $c = 14.80$ Å, and eight formula units per cell. Hodgson et al.[6] provided a much more detailed account; they assigned the space group to $P4_2/mnm$ with $a = 16.259$ (7) Å, $c = 7.411(7)$ Å, and four formula units per cell. The latter structure was refined to a conventional R value of 0.077. According to this structure the discrete $[(NH_3)_5CrOHCr(NH_3)_5]^{5+}$ complexes have exact C_{2v} symmetry. The 2-fold molecular axes lie perpendicular to the c axis of the tetragonal crystal. The complexes occupy a 4-fold crystallographic site and are therefore all equivalent. Early and preliminary spectroscopic measurements[7] provided some evidence for the existence of two inequivalent sets of complexes, in contradiction to the X-ray diffraction result.

Modern optical spectroscopic techniques allow a site-selective probing of the molecular properties.[8] The luminescence of each site can be obtained individually by selective excitation using tunable lasers. Alternatively, individual excitation spectra can be obtained by monitoring a narrow emission line of a given set. It is possible to obtain molecular parameter separately for inequivalent sites. Polarized single-crystal spectroscopic data should provide information about electronic excitations as well as molecular orientations. Energy splittings resulting from exchange interactions in the dimeric unit $[(NH_3)_5CrOHCr(NH_3)_5]^{5+}$ are of particular interest in the title compound. Since the bulk magnetic properties[6] are determined by the average electronic ground-state splittings of all the sites in the crystal, the spectroscopic probe is expected to be much more selective and thus more informative. In addition, the presence of nearly but not exactly equivalent sites can be used to investigate the nonradiative intermolecular transfer of electronic excitation energy. In this context the presence of inequivalent sites, which clearly limits the power of bulk techniques, turns out to be an advantage. The title

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