larization, and absorption factors, the last computed by the numerical integration method of Busing and Levy[22] (transmission factors between 0.26 and 0.77). The diffraction power of the crystal was poor, and weak reflections were not precise enough to allow keeping data below 3σ, so a unique data set of 1640 reflections having $I > 3\sigma(I)$ was used for determining and refining the structure.

The structure was solved with use of the heavy-atom method. After refinement of the heavy atoms, a difference-Fourier map revealed maxima of residual electronic density close to the positions expected for hydrogen atoms. They were introduced in structure factor calculations by their computed coordinates (C–H = 0.95 Å) and isotropic temperature factors of 6 Å^2 but not refined. Full least-squares refinement converged to $R(F) = 0.075$ and $R_w(F) = 0.096$ $[w = 1/\sigma_{\mathrm{count}}^2 + (pI)^2)]$. The ignorance factor p was estimated from equivalent $0kl$ and $0k\bar{l}$ intensities; for $p = 0.08$ the unit-weight observation is equal to 1.93. A final difference map revealed no significant maxima. The scattering factors of Cromer and Waber[23] and the anomalous dispersion coefficients of Cromer[24] were used in all structure factor calculations.

Registry No. **1**, 82884-19-3; **2**, 91606-21-2; **3**, 91606-16-5; **4**, 91606-17-6; **5**, 89161-57-9; **6**, 91606-18-7; **7**, 91606-19-8; **8**, 91606-20-1; (THF)Cr(CO)$_5$, 15038-41-2; W(CO)$_6$, 14040-11-0; Mo(CO)$_6$, 13939-06-5.

Supplementary Material Available: Table IV, positional and thermal parameters for hydrogen atoms, Table V, least-squares mean planes of interest, Table VI, thermal parameters for anisotropic atoms, and Table VII, observed and calculated structure factor amplitudes for all observed reflections (×10) (11 pages). Ordering information is given on any current masthead page.

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Monomeric and Anion-Bridged Dimeric and Polymeric Oxamide Oxime Complexes of Copper(II): Preparation, Crystal and Molecular Structures, and Magnetic Properties

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Received December 13, 1983

Aquabis(oxamide oxime)copper(II) sulfate, $[\mathrm{Cu(C_2H_6N_4O_2)_2(H_2O)]SO_4}$, crystallizes in the orthorhombic space group *Pbca* (D_{2h}^{15}) with 8 molecules in a unit cell of dimensions $a = 7.829$ (2) Å, $b = 12.568$ (4) Å, and $c = 28.284$ (12) Å. The structure has been refined by least-squares methods to an R_w of 0.031 for 1320 reflections. The copper ion is coordinated by four oxime nitrogen atoms and the water molecule in a square-pyramidal arrangement. The complex molecules are monomeric, and the magnetic susceptibility data obey the Curie–Weiss law $\chi = C/(T - \Theta)$ with $C = 0.442$ (1) and $\Theta = 0.68$ (1)°. Bis(μ-sulfato)bis[aqua(oxamide oxime)copper(II)], $[\mathrm{Cu(C_2H_6N_4O_2)(H_2O)(SO_4)]_2}$, crystallizes in the triclinic space group $P\bar{1}$ with 1 molecule in a unit cell of dimensions $a = 6.726$ (1) Å, $b = 7.982$ (1) Å, $c = 9.462$ Å, $\alpha = 66.93$ (1)°, $\beta = 74.37$ (1)°, and $\gamma = 68.81$ (1)°. The final R_w was 0.026 for 1457 reflections. The copper(II) ions are exchange coupled in this bimetallic complex, and the magnetic susceptibility data in the temperature range 1.4–65.7 K yield a singlet–triplet splitting of 2.55 cm^{-1}, with the singlet state being the ground state. The best fit g value was 2.19. *catena*-μ-Sulfato[diaqua(oxamide oxime)copper(II)], $[\mathrm{Cu(C_2H_6N_4O_2)(H_2O)_2(SO_4)]}_n$, crystallizes in the orthorhombic space group *Pcca* (D_{2h}^{8}) with 4 molecules in a unit cell of dimensions $a = 7.121$ (1) Å, $b = 9.734$ (2) Å, $c = 13.770$ (2) Å. The final R_w was 0.031 for 800 reflections. In the sulfato-bridged polymeric molecules, "4 + 1 + 1" distorted-octahedral coordination about copper is achieved by coordination of two nitrogens from oxamide oxime, by two oxygens from separate sulfate ions that propagate the chain, and by two water molecules. Magnetic measurements reveal antiferromagnetic exchange coupling in the unusual chain compound *catena*-dichloro(oxamide oxime)copper(II) with best fit parameters to the Heisenberg exchange model being $J = -1.0$ (1) cm^{-1} and $g = 2.12$ (1).

Introduction

Complexes of metal salts with α,β-dione dioximes (α,β-dodoH$_2$) as chelating ligands have been the object of recent interest since the nature of the complexes formed in the solid state depends on the crystallization conditions.[1,2] Monomeric,[3] dimeric,[4-9] and polymeric chain compounds[2,10-12] of the neutral ligand are known, and exchange coupling is frequently found in the oligomeric and polymeric compounds.[12-14] For example, the dimeric compound [Cu(dimethylglyoxime)Cl$_2$]$_2$ exhibits a triplet ground state,[13,14] and the chain compound [Cu(diphenylethanedione dioxime)Cl$_2$]$_n$ is an $S = {}^1/_2$ Heisenberg antiferromagnet.[12] Compounds of charged ligands and of mixed-ligand systems have also been prepared and studied recently.[15]

The ligand oxamide oxime[16] (oaoH$_2$) is of particular interest since the amino groups may also be expected to coordinate to metal ions, and in this manner polymeric compounds with short pathways for superexchange interactions may be formed. As a part of a systematic study of the coordination chemistry

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0020-1669/84/1323-3467$01.50/0

Table I. Crystallographic Data and Data Collection Summary

formula	$[Cu(C_2H_6N_4O_2)_2(H_2O)]SO_4$	$[Cu(C_2H_6N_4O_2)(H_2O)(SO_4)]_2$	$[Cu(C_2H_6N_4O_2)(H_2O)_2(SO_4)]_n$
fw	413.82	591.45 (dimer)	313.74 (monomer)
space group	*Pbca* (D_{2h}^{15})	$P\bar{1}$	*Pcca* (D_{2h}^{8})
cryst syst	orthorhombic	triclinic	orthorhombic
cell dimens (291 K)			
a, Å	7.829 (2)	6.726 (1)	7.121 (1)
b, Å	12.568 (4)	7.982 (1)	9.734 (2)
c, Å	28.284 (12)	9.462 (1)	13.770 (2)
α, deg		66.93 (1)	
β, deg		74.37 (1)	
γ, deg		68.81 (1)	
V, Å^3	2783	430.9	954.5
D_{calcd}, g cm^{-1}	1.97	2.28	2.18
Z	8	1	4
2θ max, deg	60	55	55
no. of obsd reflcns ($I \geqslant 2.5\sigma(I)$)	1320	1457	800
R_w (*R*)	0.031 (0.034)	0.026 (0.028)	0.031 (0.031)
final no. of parameters	264	168	94
radiation	Mo Kα (λ = 0.71069 Å)		
μ, cm^{-1}	18	28	24
min transmissn (max = 1)	0.83	0.83	0.75
scan type	θ/2θ	θ/2θ	θ2/θ
scan speed in 2θ, deg min^{-1}	2 (29.3)	3 (29.3)	2.5 (29.3)
scan range in 2θ, deg	1.4	1.7	1.35

of oxamide oxime with metal salts, we have prepared and characterized the following three new compounds: monomeric $[Cu(oaoH_2)_2(H_2O)]SO_4$ (**1**) in which the sulfate ion is hydrogen bonded to the cation; dimeric $[Cu(oaoH_2)(H_2O)(SO_4)]_2$ (**2**) in which the pair of copper(II) ions are bridged by the two sulfate ions; the one-dimensional chain compound $[Cu(oaoH_2)(H_2O)_2(SO_4)]_n$ (**3**) in which the copper(II) ions are bridged by one sulfate ligand, yielding the superexchange pathway $(-Cu-O-S-O-Cu-)_n$. The preparations, single-crystal X-ray diffraction structural studies, and magnetic studies are discussed here. In addition, results of magnetic studies on the unusual chain compound *catena*-dichloro (oxamide oxime)copper(II) are presented and discussed. In this chain compound, the two copper ions in the chain-propagating moiety are bridged by one chloride and perhaps by a nitrogen from the oxime ligand.[2]

Experimental Section

Synthesis. The compounds $[Cu(oaoH_2)_2(H_2O)]SO_4$ (**1**) and $[Cu(oaoH_2)(H_2O)(SO_4)]_2$ (**2**) were prepared by a diffusion technique. A sintered-glass filtration funnel was placed upside down in beaker containing water. Copper(II) sulfate (approximately 0.5 g) was dissolved in the beaker, and solid oxamide oxime (approximately 0.3 g) was put on the filter plate. After the mixture was allowed to stand for 4 weeks at room temperature, the $oaoH_2$ had dissolved and the solution had turned green. Green crystals of **1** had grown on the filter plate and were isolated by filtration.

A dull green precipitate was removed by filtration from the mother liquor in the beaker. The green solution was permitted to evaporate at room temperature, and green crystals of $[Cu(oaoH_2)(H_2O)(SO_4)]_2$ (**2**) deposited when most of the solvent had evaporated. A larger crop of **1**, which was used for magnetic measurements, was obtained when an aqueous solution of 0.5 g of $oaoH_2$ was added with stirring to a solution of 1.25 g of copper(II) sulfate in 150 mL of H_2O. After the mixture was allowed to stir overnight, an amorphous green precipitate was removed by filtration, and the green solution was allowed to evaporate at room temperature. When most of the solvent was evaporated, large green crystals of **1** together with small light green crystals of unknown composition had formed. The small crystals were removed by treating the solid with dilute sulfuric acid. The identity of the crystals of **1** obtained in this way with those from the above diffusion method was checked by comparing their lattice parameters.

For the preparation of $[Cu(oaoH_2)(H_2O)_2(SO_4)]_n$, an aqueous solution of 1.18 g of $oaoH_2$ was added slowly with stirring to an aqueous solution of 3.8 g of $CuSO_4{\cdot}5H_2O$. The solution turned green, and a green gelatinous mass formed. The mixture was stirred overnight, after which it was filtered, and the filtrate was allowed to evaporate at room temperature. A mixture of large yellow-green hexagonal plates, **3**, and small blue-green crystals formed. The blue-green crystals decomposed in air and were not identified. The yellow-green crystals of **3** were suitable for X-ray structural studies and EPR measurements, but it was not possible to collect an adequate sample for magnetic susceptibility measurements. When the syntheses of **1** and of **3** are compared, it is evident that the nature of the phase obtained depends on subtle differences in the preparations. Whereas formation of **1** and **2** by the diffusion method is well reproducible, it is not completely clear which factors favor the precipitation of **1** or **3** from the combined solutions of the reactants. The preparation of *catena*-dichloro(oxamide oxime)copper(II) has been described elsewhere.[2]

Magnetic Measurements. Magnetic susceptibility data were collected on powdered samples of $[Cu(oaoH_2)_2(H_2O)]SO_4$ and $[Cu(oaoH_2)(H_2O)(SO_4)]_2$ on a Princeton Applied Research Model 155 vibrating sample magnetometer (VSM), which was operated from zero field to 10 kOe by using procedures that have been described previously.[17] The VSM magnet (Magnion H-96), power supply (Magnion HSR-1365), and associated field control unit (Magnion FFC-4 with a Rawson-Lush Model 920 MCM rotating-coil gaussmeter) were calibrated against NMR resonances (^{1}H and ^{3}Li).

The VSM magnetometer was calibrated with $HgCo(NCS)_4$.[18] Powdered samples of the compound and calibrant used in this study were contained in precision-milled Lucite sample holders. Approximately 150 mg of each was used. Diamagnetic corrections for the constituent atoms were made with Pascal's constants, and corrections for temperature-independent paramagnetism were estimated from tabulated data.[19-21]

EPR Measurements. Electron paramagnetic resonance spectra were recorded with a B-ER 418 Bruker EPR spectrometer. The microwave frequency was measured with a Bruker EIP-320D frequency counter, and the magnetic field strength was determined with a Fa. Bruker nuclear resonance gaussmeter. Relative line intensities were obtained by double integration of the EPR spectra on an ASPECT 2000 computer from Fa. Bruker.

X-ray Crystallographic Studies. For the X-ray structural determinations, crystals were mounted on glass capillaries and reflection measurements were made at room temperature. Cell dimensions were determined from the setting angles of 25 reflections on a Syntex R3 diffractometer equipped with a molybdenum X-ray tube and a graphite monochromator. Pertinent crystallographic data for the three com-

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Table II. Atomic Positions (×10^4, Hydrogen Positions ×10^3) and Isotropic Temperature Factors (×10^3) Equivalent to the Refined Anisotropic Values for [Cu(oaoH$_2$)$_2$(H$_2$O)] SO$_4$ (1)[a]

atom	*x*	*y*	*z*	U_{eq}, Å^2
Cu	4102.5 (8)	−476.9 (5)	6353.9 (2)	26.8 (2)
N(1)	4970 (5)	−1581 (3)	6805 (1)	26 (1)
N(2)	3349 (6)	117 (3)	6979 (1)	31 (2)
N(3)	2868 (5)	561 (3)	5975 (1)	28 (1)
N(4)	4334 (5)	−1091 (3)	5691 (1)	26 (1)
N(5)	5157 (7)	−2059 (3)	7596 (1)	46 (2)
N(6)	3516 (7)	−90 (4)	7799 (2)	43 (2)
N(7)	1656 (6)	967 (4)	5245 (1)	37 (2)
N(8)	3319 (6)	−948 (3)	4913 (1)	37 (2)
O(1)	5749 (5)	−2581 (3)	6737 (1)	36 (1)
O(2)	2532 (5)	1073 (3)	7085 (1)	42 (1)
O(3)	2113 (6)	1513 (4)	6140 (2)	37 (2)
O(4)	5113 (6)	−2012 (3)	5510 (1)	34 (1)
C(1)	4704 (7)	−1400 (4)	7251 (2)	28 (2)
C(2)	3804 (6)	−397 (4)	7354 (2)	25 (2)
C(3)	2560 (7)	354 (4)	5531 (2)	24 (2)
C(4)	3448 (6)	−624 (4)	5364 (2)	25 (2)
O(5)	6621 (6)	496 (4)	6338 (2)	38 (1)
S	4379 (2)	−1655 (1)	9023.3 (4)	26.7 (4)
O(6)	2892 (5)	−2392 (3)	8987 (1)	45 (1)
O(7)	5641 (5)	−2191 (3)	9320 (1)	53 (2)
O(8)	3802 (5)	−665 (3)	9249 (1)	39 (1)
O(9)	5054 (6)	−1441 (3)	8555 (1)	62 (2)
H(1)	650 (5)	−248 (3)	654 (1)	25 (12)
H(2)	219 (6)	131 (3)	687 (1)	33 (13)
H(3)	275 (9)	186 (5)	606 (3)	79 (32)
H(4)	591 (7)	−220 (4)	564 (2)	29 (3)
H(5)	563 (5)	−260 (3)	754 (2)	45 (14)
H(6)	506 (6)	−191 (3)	788 (2)	34 (13)
H(7)	400 (8)	−31 (5)	803 (2)	103 (23)
H(8)	292 (8)	47 (4)	783 (2)	69 (23)
H(9)	389 (7)	−152 (4)	480 (2)	79 (19)
H(10)	269 (6)	−63 (4)	477 (1)	43 (15)
H(11)	151 (6)	85 (4)	497 (2)	28 (17)
H(12)	131 (5)	154 (3)	534 (1)	30 (13)
H(13)	660 (8)	100 (4)	629 (2)	46 (26)
H(14)	727 (6)	16 (4)	615 (2)	48 (15)

[a] U_{eq} is defined as one-third of the trace of the orthogonalized U_{ij} matrix. The refined isotropic values of *U* are given for hydrogen atoms.

pounds in this study are given in Table I along with the details concerning data collection. Reflections used in the structural determinations were those with an intensity $I > 2.5\sigma(I)$. These were corrected for Lorentz and polarization factors, and an empirical absorption correction (Ψ scans) was made.

The structures were solved by locating the copper ions from Patterson functions, and the positions of the remaining non-hydrogen atoms were obtained from Fourier syntheses. After refinement of these atom positions with anisotropic temperature factors, the positions of the hydrogen atoms were determined from difference Fourier syntheses. The hydrogen atoms were refined with isotropic temperature factors. Refinements were carried out by the cascade-matrix least-squares procedure using a NOVA 3 computer with the program system SHELXTL.[22] The program uses scattering factors from ref 23 and takes anomalous dispersion into account. The function minimized was

$$\sum w^{1/2}(|F_o| - |F_c|)$$

where weights, *w*, were taken to be $1/\sigma^2(F)$. The final discrepancy indices given in Table I were defined as

$$R = \sum||F_o| - |F_c||/\sum|F_o|$$

$$R_w = \sum(w^{1/2}||F_o| - |F_c||)/\sum w^{1/2}|F_o|$$

Fractional coordinates are given in Table II for 1, Table IV for 2, and Table VI for 3. Tables of thermal parameters and calculated and observed structure amplitudes are deposited as supplmentary material. Drawings of the structures were made with a Tektronix plotter in conjunction with a plotting routine from SHELXTL. The atom-numbering schemes are shown in Figure 1 for 1, Figure 2 for 2, and Figure 3 for 3.

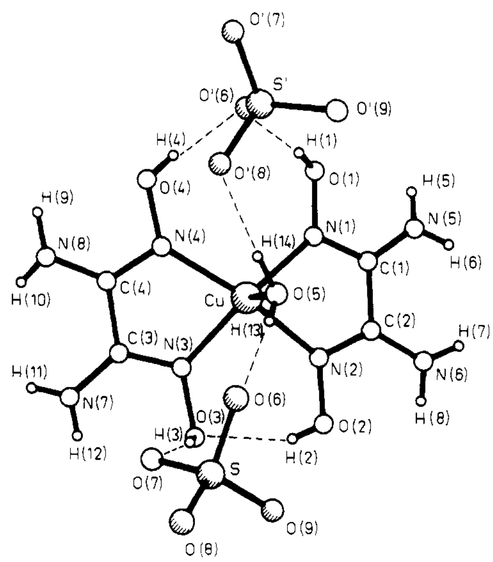

Figure 1. View of the structure of the complex cation and two sulfate ions in [Cu(oaoH$_2$)$_2$(H$_2$O)]SO$_4$ (1). Hydrogen bonds are indicated by dashed lines, and bond distances and angles are given in Table II.

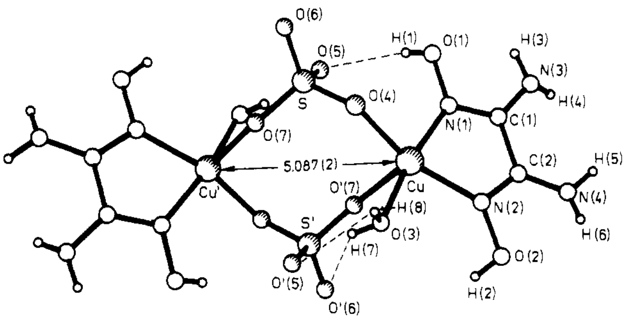

Figure 2. View of the structure of the centrosymmetric dimeric molecule [Cu(oaoH$_2$)(H$_2$O)(SO$_4$)]$_2$ (2).

Results and Discussion

Description of the Structure of [Cu(oaoH$_2$)$_2$(H$_2$O)]SO$_4$. As shown in Figure 1, coordination of the copper(II) ion in [Cu(oaoH$_2$)$_2$(H$_2$O)]SO$_4$ is distorted tetragonal pyramidal, with the base of the pyramid being formed by four oxime nitrogen atoms. An oxygen atom from the water molecule occupies the apical position of the tetragonal pyramid. The copper–nitrogen and copper–oxygen bond distances given in Table III are typical. The copper ion lies 0.16 Å above the plane formed by the four nitrogen atoms. The oxime ligands are not ionized and are coordinated as neutral ligands.

There is *only one* intramolecular hydrogen bond formed between oxime ligands in the molecule, that being [O(2)–H(2)···O(3)]. As shown in Figure 1, the other oxime hydrogen H(3) forms a hydrogen bond with a sulfate counterion. There is no intramolecular hydrogen bond on the other side of the molecule, thus resulting in an unsymmetrical structure for the complex cation. H(1) and H(4) are hydrogen bonded to one oxygen of an adjacent sulfate counterion, forming a closed cyclic system. Similar cyclic hydrogen-bonding arrangements have been observed in oxamide oxime complexes of palladium(II) and platinum(II).[24,25]

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Table III. Bond Lengths (Å) and Angles (deg) for $[Cu(oaoH_2)_2(H_2O)]SO_4$ (1)

(a) Bond Lengths

Cu-N(1)	2.003 (4)	N(7)-C(3)	1.322 (6)	O(5)-O(6)	2.835 (6)
Cu-N(2)	2.009 (4)	N(7)-H(11)	0.79 (5)	O(5)-O'(8)	2.792 (6)
Cu-N(3)	1.945 (4)	N(7)-H(12)	0.81 (4)	H(2)-O(3)	2.09 (4)
Cu-N(4)	2.034 (4)	N(8)-C(4)	1.345 (6)	H(1)-O'(6)	1.85 (4)
Cu-O(5)	2.320 (4)	N(8)-H(9)	0.90 (5)	H(3)-O(7)	2.04 (7)
N(1)-O(1)	1.411 (5)	N(8)-H(10)	0.75 (5)	H(4)-O'(6)	1.89 (5)
N(1)-C(1)	1.299 (6)	C(1)-C(2)	1.473 (7)	H(13)-O(6)	2.21 (5)
N(2)-O(2)	1.394 (5)	C(3)-C(4)	1.489 (7)	H(14)-O'(8)	1.95 (5)
N(2)-C(2)	1.291 (6)	O(1)-H(1)	0.82 (4)	S-O(6)	1.491 (4)
N(3)-O(3)	1.415 (6)	O(2)-H(2)	0.72 (4)	S-O(7)	1.460 (4)
N(3)-C(3)	1.304 (6)	O(3)-H(3)	0.70 (7)	S-O(8)	1.469 (4)
N(4)-O(4)	1.405 (5)	O(4)-H(4)	0.77 (5)	S-O(9)	1.452 (4)
N(4)-C(4)	1.297 (6)	O(5)-H(13)	0.65 (5)	N(7)-O''(8)	2.865 (5)
N(5)-C(1)	1.327 (6)	O(5)-H(14)	0.84 (5)	H(11)-O''(8)	2.07 (5)
N(5)-H(5)	0.79 (4)	O(2)-O(3)	2.747 (5)	N(5)-O'''(9)	2.822 (5)
N(5)-H(6)	0.84 (4)	O(1)-O'(6)	2.658 (5)	H(6)-O'''(9)	1.99 (4)
N(6)-C(2)	1.335 (6)	O(3)-O(7)	2.727 (6)	N(6)-O'''(9)	2.984 (6)
N(6)-H(7)	0.81 (6)	O(4)-O'(6)	2.643 (6)	H(7)-O'''(9)	2.21 (6)
N(6)-H(8)	0.86 (6)				

(b) Bond Angles

N(1)-Cu-N(2)	78.2 (2)	C(2)-N(6)-H(8)	116 (4)	H(11)-N(7)-H(12)	116 (5)
N(1)-Cu-N(3)	169.6 (2)	C(3)-N(7)-H(11)	124 (4)	H(9)-N(8)-H(10)	125 (5)
N(1)-Cu-N(4)	107.1 (2)	C(3)-N(7)-H(12)	119 (3)	H(13)-O(5)-H(14)	111 (6)
N(1)-Cu-O(5)	95.1 (2)	C(4)-N(8)-H(9)	122 (3)	N(1)-O(1)-H(1)	105 (3)
N(2)-Cu-N(3)	95.2 (2)	C(4)-N(8)-H(10)	113 (3)	N(2)-O(2)-H(2)	110 (3)
N(2)-Cu-N(4)	168.0 (2)	O(1)-N(1)-C(1)	110.9 (4)	N(3)-O(3)-H(3)	97 (6)
N(2)-Cu-O(5)	94.1 (2)	O(2)-N(2)-C(2)	112.5 (4)	N(4)-O(4)-H(4)	115 (4)
N(3)-Cu-N(4)	77.9 (2)	O(3)-N(3)-C(3)	114.2 (4)	N(1)-C(1)-N(5)	124.2 (5)
N(3)-Cu-O(5)	93.3 (2)	O(4)-N(4)-C(4)	110.2 (4)	N(1)-C(1)-C(2)	114.7 (4)
N(4)-Cu-O(5)	96.1 (2)	O(6)-S-O(7)	106.4 (2)	N(5)-C(1)-C(2)	121.1 (4)
Cu-N(1)-O(1)	132.6 (3)	O(6)-S-O(8)	108.5 (2)	N(2)-C(2)-N(6)	125.6 (5)
Cu-N(1)-C(1)	116.3 (3)	O(6)-S-O(9)	109.6 (2)	N(2)-C(2)-C(1)	113.5 (4)
Cu-N(2)-O(2)	130.0 (3)	O(7)-S-O(8)	110.4 (2)	N(6)-C(2)-C(1)	120.9 (4)
Cu-N(2)-C(2)	117.1 (3)	O(7)-S-O(9)	111.3 (3)	N(3)-C(3)-N(7)	124.9 (4)
Cu-N(3)-O(3)	126.3 (3)	O(8)-S-O(9)	110.6 (2)	N(3)-C(3)-C(4)	112.5 (4)
Cu-N(3)-C(3)	119.3 (3)	O(2)-H(2)-O(3)	153 (4)	N(7)-C(3)-C(4)	122.5 (4)
Cu-N(4)-O(4)	133.4 (3)	O(1)-H(1)-O'(6)	168 (4)	N(4)-C(4)-N(8)	125.5 (4)
Cu-N(4)-C(4)	116.0 (3)	O(3)-H(3)-O(7)	168 (7)	N(4)-C(4)-C(3)	113.4 (4)
Cu-O(5)-H(13)	120 (6)	O(4)-H(4)-O'(6)	169 (6)	N(8)-C(4)-C(3)	121.1 (4)
Cu-O(5)-H(14)	105 (3)	O(5)-H(13)-O(6)	166 (7)	N(7)-H(11)-O''(8)	176 (6)
C(1)-N(5)-H(5)	121 (4)	O(5)-H(14)-O'(8)	176 (4)	N(5)-H(6)-O'''(9)	174 (5)
C(1)-N(5)-H(6)	123 (3)	H(5)-N(5)-H(6)	116 (5)	N(6)-H(7)-O'''(9)	159 (5)
C(2)-N(6)-H(7)	126 (4)	H(7)-N(6)-H(8)	117 (6)		

Table IV. Atomic Positions ($\times 10^4$, Hydrogen Positions $\times 10^3$) and Isotropic Temperature Factors ($\times 10^3$) for $[Cu(oaoH_2)(H_2O)(SO_4)]_2$ (2)

atom	*x*	*y*	*z*	U_{eq}, Å^2
Cu	7280.9 (8)	10846.3 (6)	2250.3 (5)	18.9 (2)
N(1)	7891 (5)	8766 (4)	4218 (3)	22 (1)
N(2)	6974 (5)	12288 (4)	3639 (3)	22 (1)
O(1)	8375 (6)	6820 (4)	4555 (3)	31 (1)
O(2)	6387 (6)	14238 (4)	3356 (3)	36 (1)
C(1)	7659 (6)	9225 (5)	5430 (4)	18 (1)
C(2)	7107 (5)	11325 (5)	5092 (4)	18 (1)
N(3)	7774 (6)	8002 (5)	6879 (3)	28 (2)
N(4)	6855 (6)	12045 (5)	6200 (3)	31 (2)
O(3)	6278 (4)	13122 (3)	534 (3)	24 (1)
S	8349 (1)	7877 (1)	610 (1)	16.2 (3)
O(4)	6741 (4)	9274 (3)	1343 (3)	23 (1)
O(5)	10083 (4)	6746 (3)	1581 (3)	22 (1)
O(6)	7242 (4)	6636 (3)	535 (3)	24 (1)
O(7)	9229 (4)	8901 (3)	−969 (2)	23 (1)
H(1)	882 (9)	661 (7)	394 (5)	57 (18)
H(2)	669 (9)	1475 (7)	247 (6)	77 (19)
H(3)	831 (6)	673 (5)	701 (4)	43 (12)
H(4)	804 (6)	825 (5)	744 (4)	21 (11)
H(5)	676 (8)	1139 (7)	719 (6)	72 (17)
H(6)	645 (9)	1308 (7)	608 (6)	61 (17)
H(7)	510 (6)	1316 (5)	23 (4)	28 (11)
H(8)	719 (6)	1315 (5)	−14 (4)	34 (11)

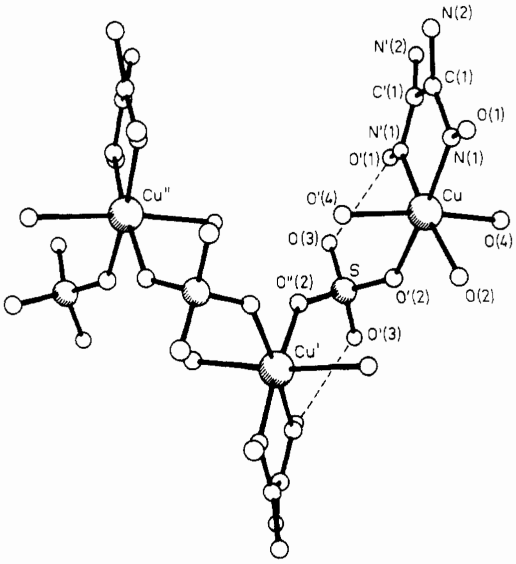

Figure 3. Portion of the chain structure of $[Cu(oaoH_2)(H_2O)_2(SO_4)]_n$ (3). Hydrogen atoms were omitted for clarity. Cu and Cu″ are related by a translation along *a*. The shortest copper–copper internuclear separation is 5.004 (2) Å.

Hydrogen atoms on the apical water molecule also form hydrogen bonds with oxygen atoms of sulfate counterions as shown by the dashed lines in Figure 1. Further hydrogen bonds link the sulfate ions, which are all crystallographically equivalent with adjacent molecules (distances and angles are included in Table IIIa,b): O(8) is connected with amino N(7)

Table V. Bond Lengths (Å) and Angles (deg) for $[Cu(oaoH_2)(H_2O)(SO_4)]_2$ (**2**)

(a) Bond Lengths

Cu–N(1)	1.972 (2)	C(2)–N(4)	1.329 (6)
Cu–N(2)	1.990 (4)	N(3)–H(3)	0.91 (4)
Cu–O(3)	1.945 (2)	N(3)–H(4)	0.72 (5)
Cu–O(4)	1.946 (3)	N(4)–H(5)	0.88 (5)
Cu–O′(7)	2.375 (3)	N(4)–H(6)	0.75 (5)
N(1)–O(1)	1.387 (4)	S–O(4)	1.491 (3)
N(1)–C(1)	1.290 (5)	S–O(5)	1.478 (3)
N(2)–O(2)	1.392 (4)	S–O(6)	1.469 (3)
N(2)–C(2)	1.295 (4)	S–O(7)	1.472 (2)
O(1)–H(1)	0.64 (5)	O(1)–O(5)	2.753 (4)
O(2)–H(2)	0.78 (4)	O(3)–O′(5)	2.719 (3)
O(3)–H(7)	0.90 (5)	O(3)–O′(6)	2.734 (5)
O(3)–H(8)	0.76 (3)	H(1)–O(5)	2.14 (5)
C(1)–C(2)	1.498 (5)	H(7)–O′(6)	1.84 (5)
C(1)–N(3)	1.339 (4)	H(8)–O′(5)	1.97 (4)

(b) Bond Angles

N(1)–Cu–N(2)	78.6 (1)	N(2)–C(2)–N(4)	125.8 (3)
N(1)–Cu–O(3)	170.0 (1)	C(1)–C(2)–N(4)	121.5 (3)
N(1)–Cu–O(4)	94.0 (1)	C(1)–N(3)–H(3)	118 (2)
N(1)–Cu–O′(7)	102.7 (1)	C(1)–N(3)–H(4)	119 (3)
N(2)–Cu–O(3)	93.9 (1)	H(3)–N(3)–H(4)	113 (4)
N(2)–Cu–O(4)	161.3 (1)	C(2)–N(4)–H(5)	124 (4)
N(2)–Cu–O′(7)	95.2 (1)	C(2)–N(4)–H(6)	123 (4)
O(3)–Cu–O(4)	91.1 (1)	H(5)–N(4)–H(6)	110 (5)
O(3)–Cu–O′(7)	84.5 (1)	Cu–O(3)–H(7)	114 (2)
O(4)–Cu–O′(7)	103.2 (1)	Cu–O(3)–H(8)	107 (2)
Cu–N(1)–O(1)	129.5 (3)	H(7)–O(3)–H(8)	109 (4)
Cu–N(1)–C(1)	117.6 (2)	O(4)–S–O(5)	108.6 (2)
O(1)–N(1)–C(1)	112.6 (2)	O(4)–S–O(6)	108.1 (2)
Cu–N(2)–O(2)	130.4 (2)	O(4)–S–O(7)	109.5 (1)
Cu–N(2)–C(2)	117.2 (3)	O(5)–S–O(6)	110.2 (1)
O(2)–N(2)–C(2)	112.0 (3)	O(5)–S–O(7)	110.7 (1)
N(1)–O(1)–H(1)	109 (4)	O(6)–S–O(7)	109.7 (2)
N(2)–O(2)–H(2)	109 (4)	Cu–O(4)–S	128.1 (2)
N(1)–C(1)–C(2)	113.4 (3)	Cu–O′(7)–S′	134.7 (1)
N(1)–C(1)–N(3)	125.0 (4)	O(1)–H(1)–O(5)	164 (6)
C(2)–C(1)–N(3)	121.4 (4)	O(3)–H(7)–O′(6)	175 (3)
N(2)–C(2)–C(1)	112.7 (4)	O(3)–H(8)–O′(5)	167 (5)

Table VI. Atomic Positions ($\times 10^4$, Hydrogen Positions $\times 10^3$) and Isotropic Temperature Factors ($\times 10^3$) for $[Cu(oaoH_2)(H_2O)(SO_4)]_n$ (3)

atom	x	y	z	U_{eq}, Å^2
Cu	0	1805.9 (6)	2500	17.6 (2)
N(1)	602 (5)	3398 (3)	3364 (2)	20 (1)
N(2)	−26 (6)	5745 (3)	3553 (3)	27 (1)
O(1)	747 (5)	3385 (3)	4384 (2)	30 (1)
C(1)	150 (7)	4606 (3)	3038 (2)	18 (1)
S	2500	0	4004.8 (9)	15.3 (3)
O(2)	849 (4)	291 (2)	3374 (2)	19 (1)
O(3)	2945 (4)	1207 (3)	4600 (2)	23 (1)
O(4)	−2899 (5)	1690 (3)	3385 (2)	25 (1)
H(1)	160 (12)	254 (8)	447 (6)	164 (35)
H(2)	23 (8)	578 (4)	420 (4)	51 (16)
H(3)	−57 (6)	645 (4)	340 (3)	26 (13)
H(4)	−361 (8)	103 (5)	331 (4)	57 (19)
H(5)	−268 (8)	160 (4)	390 (3)	34 (15)

by H(11), and O(9) is connected with amino N(5) and N(6) by H(6) and H(7) of different adjacent molecules. Thus, the sulfate oxygen atoms are engaged in hydrogen bonds to different complex molecules, and an extended three-dimensional H-bonding network runs through the crystal.

Magnetic Properties of $[Cu(oaoH_2)_2(H_2O)]SO_4$. Since the complex cations in $[Cu(oaoH_2)_2(H_2O)]SO_4$ are linked by hydrogen bonding into a three-dimensional network, a study of the magnetic properties of **1** was undertaken to determine whether the copper(II) ions were exchange coupled. Magnetic data are plotted as inverse susceptibility vs. temperature in Figure 1S (supplementary material). The magnetic susceptibility data obey the Curie–Weiss law $\chi = C/(T - \Theta)$, with the best fit parameters from a nonlinear Simplex fitting routine being $C = 0.442$ (1) and $\Theta = 0.68$ (1)°. The solid line in Figure 1S (supplementary material) was generated with the best fit magnetic parameters. The criterion of best fit in the Simplex fitting routine was the minimum value of the function

$$\sum_i (\chi_i^{calcd} - \chi_i^{obsd})^2/(\chi_i^{obsd})^2$$

A g value of 2.17 may be calculated from the Curie constant by using the equation $g^2 = CkS(S + 1)/3N\mu_B^2$.

Studies of EPR line widths on single crystals of $[Cu(oaoH_2)_2(H_2O)]SO_4$ may reveal the presence of magnetic coupling, since it is well-known that hydrogen bonding such as that present in **1** provides effective superexchange pathways for exchange interactions. However, the magnetic susceptibility data indicate that any magnetic interactions present must be very small.

Description of the Structure of $[Cu(oaoH_2)(H_2O)(SO_4)]_2$. The structure of the dimeric, centrosymmetric molecule $[Cu(oaoH_2)(H_2O)(SO_4)]_2$ is shown in Figure 2, where it may be seen that the copper(II) ions are bridged by two sulfate ions, resulting in Cu–O–S–O–Cu bridged linkages. Coordination about copper is distorted tetragonal pyramidal, with the base being formed by two nitrogen atoms from the neutral oxamide oxime ligand, an oxygen atom from one of the two bridging sulfate ions, and an oxygen atom from the water molecule. The apex of the distorted tetragonal pyramid is occupied by an oxygen from the second bridging sulfate. The copper(II) ions lies 0.22 Å above the basal plane, and the copper–copper internuclear distance in the dimer is 5.087 Å.

There is significant intramolecular hydrogen bonding involving the hydrogens of the water molecule and bridging sulfate ligands. These bonds are shown by the dashed lines in Figure 2, and the pertinent distances are given in Table V.

The dimeric compound $[Cu(oaoH_2)(H_2O)(SO_4)]_2$ has the typical parallel–planar structure in which the bridging ligand occupies a basal position in the coordination sphere of one copper ion and an apical position in the coordination sphere of the second copper ion in the dimer. Typically, the in-plane bond to the first copper is short (being 1.946 Å in **2**), and the out-of-plane bond in the apical position of the second copper is somewhat longer [Cu–O′(7) = 2.375 (3) Å]. However, in this case there is an extended bridging linkage, with one oxygen of a bridging sulfate being coordinated in the basal plane of one copper, and a second oxygen of that sulfate ion occupies the apical position of the second copper ion. The superexchange pathways are Cu–O(4)–S–O(7)···Cu′ and Cu–O′(7)–S–O′(4)···Cu′. The in-plane copper–oxygen bond distance has a typical value, but the out-of-plane bond distance is rather short and, as a result, exchange coupling may be anticipated even though the superexchange pathway is rather long. The magnetic studies described in the next section confirm this supposition.

Magnetic Properties of $[Cu(oaoH_2)(H_2O)(SO_4)]_2$. Magnetic susceptibility data for $[Cu(oaoH_2)(H_2O)(SO_4)]_2$ are plotted vs. temperature in Figure 4, where it may be seen that the susceptibility data exhibit a maximum value at 2.4 K that is characteristic of antiferromagnetic exchange interactions. Assuming pairwise Heisenberg exchange described by the Hamiltonian

$$\mathcal{H} = -2J\hat{S}_1 \cdot \hat{S}_2$$

the equation for the magnetic susceptibility per mole of copper is

$$\chi_M = [Ng^2\mu_B^2/3kT][1 + \tfrac{1}{3}\exp(-2J/kT)]^{-1}$$

The equation was fit to the experimental data with a nonlinear Simplex fitting routine, and the solid line in Figure 4 shows

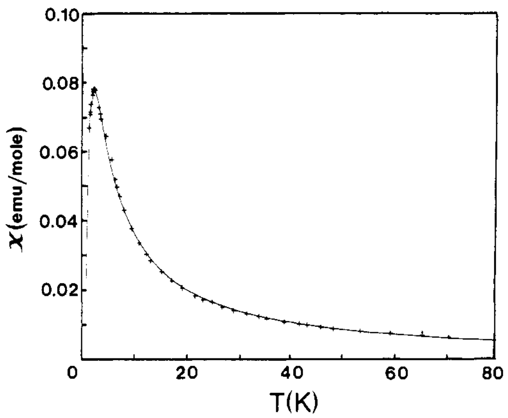

Figure 4. Magnetic susceptibility data for $[Cu(oaoH_2)(H_2O)(SO_4)]_2$ (**2**). The solid line was generated by the best fit parameters to the theoretical expression for pairwise Heisenberg exchange coupling of two $S = {}^1/_2$ ions. Data are given per mole of copper.

Table VII. Bond Lengths (Å) and Angles (deg) for $[Cu(oaoH_2)(H_2O)(SO_4)]_n$ (3)

(a) Bond Lengths

Cu-N(1)	2.000 (3)	N(2)-H(3)	0.82 (4)
Cu-O(2)	1.997 (2)	O(1)-H(1)	1.03 (8)
Cu-O(4)	2.400 (3)	C(1)-C′(1)	1.497 (7)
N(1)-O(1)	1.409 (4)	S-O(2)	1.489 (3)
N(1)-C(1)	1.299 (4)	S-O(3)	1.466 (3)
N(2)-C(1)	1.322 (5)	O(4)-H(4)	0.83 (5)
N(2)-H(2)	0.91 (5)	O(4)-H(5)	0.73 (5)

(b) Bond Angles

N(1)-Cu-O(2)	98.6 (1)	H(2)-N(2)-H(3)	108 (4)
N(1)-Cu-O(4)	85.4 (1)	N(1)-O(1)-H(1)	100 (4)
N(1)-Cu-N′(1)	78.4 (2)	N(1)-C(1)-N(2)	126.7 (3)
N(1)-Cu-O′(2)	174.5 (1)	N(1)-C(1)-C′(1)	122.2 (2)
N(1)-Cu-O′(4)	98.9 (1)	N(2)-C(1)-C′(1)	121.1 (2)
O(2)-Cu-O(4)	85.4 (1)	O(2)-S-O(3)	110.1 (1)
O(2)-Cu-O′(2)	84.8 (1)	O(2)-S-O′(2)	108.6 (2)
O(2)-Cu-O′(4)	90.6 (1)	O(2)-S-O′(3)	107.9 (1)
O(4)-Cu-O′(4)	174.6 (1)	O(3)-S-O′(3)	112.1 (2)
Cu-N(1)-O(1)	127.0 (2)	Cu-O(2)-S	127.0 (2)
Cu-N(1)-C(1)	116.3 (2)	Cu-O(4)-H(4)	120 (4)
O(1)-N(1)-C(1)	111.8 (3)	Cu-O(4)-H(5)	108 (4)
C(1)-N(2)-H(2)	122 (3)	H(4)-O(4)-H(5)	100 (5)
C(1)-N(2)-H(3)	128 (3)		

the result of the best fit using the parameters $2J = -2.55$ cm^{-1} and $g = 2.19$.

EPR of $[Cu(oaoH_2)(H_2O)(SO_4)]_2$. The EPR spectrum of polycrystalline $[Cu(oaoH_2)(H_2O)(SO_4)]_2$ exhibits the typical spectrum of a compound with an axial g factor, with $g_{\parallel} = 2.291$ and $g_{\perp} = 2.073$. There was no structure on the EPR lines due to hyperfine interactions. The temperature dependence of the EPR line intensity followed the Curie–Weiss law between 110 and 315 K as expected since these temperatures are large with respect to the singlet–triplet splitting.

Description of the Structure of $[Cu(oaoH_2)(H_2O)_2(SO_4)]_n$. The asymmetric unit consist of half of the monomeric unit, with the other half being generated by a twofold rotation about an axis through the copper and the middle of the carbon–carbon bond. The atomic coordinates are listed in Table VI, and the bond angles and bond lengths are given in Table VIIa,b. A portion of the chain structure is shown in Figure 3. The coordination about copper is distorted-octahedral "4 + 2", with two nitrogen atoms from the neutral oxamide oxime ligand and two oxygen atoms from bridging sulfate ions forming the basal plane. The apical positions are occupied by oxygen atoms from water molecules. In an analogous manner to that seen in the structure of the dimeric molecule $[Cu(oaoH_2)(H_2O)(SO_4)]_2$ the bridging sulfate ligand is bonded by one oxygen to each of two adjacent copper ions. Sulfate-bridged copper(II) chains are rare.[26] The chain that is formed lies parallel to the a axis. The copper–copper internuclear separation in the chain is 5.004 (2) Å, a value that is similar to the copper–copper separation of 5.087 (2) Å in the dimeric molecule. This is an unexpected similarity since the bridging sulfate oxygens occupy axial–basal sites in the dimer and basal–basal sites in the chain compound. The distances may be understood in terms of the smaller O–S–O angle of 108.6° in the chain and 109.5° in the dimer.

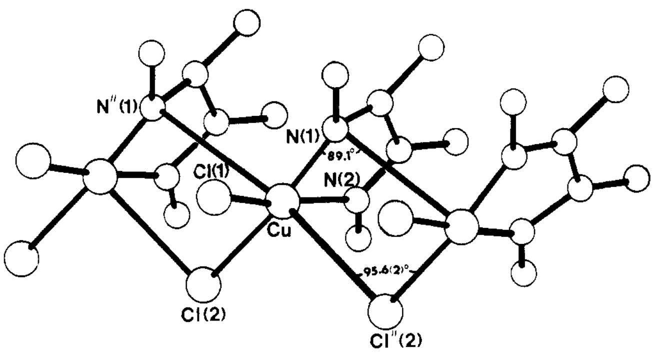

Figure 5. Structure of the chain compound *catena*-dichloro(oxamide oxime)copper(II). See ref 2.

The hydrogen atoms of the oxamide oxime ligands are hydrogen bonded to the non-copper-bonded oxygens of the bridging sulfate ligand. The pertinent bond distances and angles are O(3)–O′(1) = 2.653 (4) Å, O(3)–H′(1) = 1.62 (8) Å, and O(3)–H′(1)–O′(1) = 180 (9)°.

EPR of $[Cu(oaoH_2)(H_2O)_2(SO_4)]_n$. The EPR spectrum at 115 K exhibits an asymmetric line centered at $g = 2.155$ with a line width of 262 G. The intensity of the EPR line follows the Curie–Weiss law in the temperature region 110–315 K. Unfortunately, it was not possible to prepare an adequate sample for magnetic susceptibility measurements, and facilities for low-temperature EPR are not available to us. Therefore, there is no experimental evidence for exchange coupling in the chain compound. However, the sulfate ion is known from the work on the dimeric molecule $[Cu(oaoH_2)(H_2O)(SO_4)]_2$ to provide a pathway for superexchange, and since the sulfate ion bridges basal sites in the chain, we have the opinion that additional experimental work will reveal that the copper ions are exchange coupled, probably with a larger exchange coupling constant than observed in the dimeric molecule.

Magnetic Properties of $[Cu(oaoH_2)Cl_2]_n$. The structure of the unusual chain compound *catena*-dichloro(oxamide oxime)copper(II) is shown in Figure 5, where it may be seen that copper ions are bridged by a chloride ion and perhaps by a nitrogen atom from the oxime ligand. This is an unusual bridging network. In view of the electronic structure of the nitrogen atom N(1) and the long Cu–N(1) interatomic separation [3.223 (20) Å], it may be argued that there is no significant copper–nitrogen interaction and that the chain should be considered to be a mono(μ-chloro)-bridged copper(II) chain compound. However, is well-known that exchange interactions may be transmitted over long copper–apical ligand distances,[27] and such a view may not be borne out by further experimental results.

Magnetic measurements were made on a small sample of the compound with the vibrating-sample magnetometer, and the magnetic susceptibilities shown in Figure 2S (supplementary material) were obtained by normalizing the magnetometer output to the EPR g value of 2.12.[2] The solid line in Figure 2S is the best fit of the Heisenberg chain model[28,29]

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(26) Hatfield, W. E.; Estes, W. E.; Marsh, W. E.; Pickens, M. W.; ter Haar, L. W.; Weller, R. R. in "Extended Linear Chain Compounds"; Miller, J. S., Ed.; Plenum Press: New York; 1982; Vol. 3, Chapter 2, pp 43–142.

(27) Hatfield, W. E. *Comments Inorg. Chem.* **1981**, *1*, 105–121.

for the antiferromagnetically exchange coupled $S = {}^1/_2$ ions with $J = -1.0$ (1) cm^{-1} and $g = 2.12$ (2). These results will now be examined in view of the magnetostructural correlations that are being developed.[27]

The ϕ/R_0 value for the Cu–Cl–Cu segment of the chain is 34.4° Å^{-1}. (The Cu–Cl–Cu angle is 95.6 (2)°, and the long Cu–Cl bond distance is 2.776 (6) Å.) This ϕ/R_0 value is intermediate between those found for bis(μ-chloro)-bridged and mono(μ-chloro)-bridged copper(II) chains.[27] A ϕ/R_0 value of 34.4 for a bis(μ-chloro)-bridged copper(II) dimer would lead to the prediction of a small negative exchange coupling constant for the Cu–Cl–Cu segment of the chain, as observed.

There are no nitrogen bridged chain precedents with which the ϕ/R_0 value for the Cu–N–Cu segment may be compared. On the basis of the Cu–N–Cu angle of 89.1°, a ferromagnetic exchange may be expected.

Conclusions. Three new compounds of the neutral ligand oxamide oxime have been prepared and characterized. The neutral ligand is involved in inter- and intramolecular hydrogen bonding, although the intermolecular hydrogen bonding in the monomeric compound $[Cu(oaoH_2)_2(H_2O)]SO_4$ does not lead to detectable exchange coupling. The new dimeric compound has bis(μ-sulfato) bridges, which are rare. This work demonstrates that the sulfate bridging ligand provides an effective pathway for superexchange interactions. The singlet–triplet splitting in $[Cu(oaoH_2)(H_2O)(SO_4)]_2$ is 2.55 cm^{-1}. It is anticipated that exchange coupling may be detected in the μ-sulfato-bridged chain compound $[Cu(oaoH_2)(H_2O)(SO_4)]_n$, however, it was not possible to prepare an adequate quantity of sample for magnetic susceptibility measurements. Magnetic susceptibility measurements revealed the presence of exchange coupling in $[Cu(oaoH_2)Cl_2]_\infty$, and once adequate data on similar compounds are available, it should be possible to determine from magnetostructural correlations whether the compound should be described as a mono(μ-chloro)-bridged copper(II) chain or a (μ-chloro,μ-nitrogen)-bridged chain.

Acknowledgment. This research was supported by the Fonds der Chemischen Industrie and the National Science Foundation through Grant No. CHE 83 08129.

Registry No. 1, 91743-23-6; **2**, 91743-24-7; **3**, 91743-26-9; $[Cu(oaoH_2)Cl_2]_n$, 91743-28-1.

Supplementary Material Available: Figures of magnetic susceptibility data for $[Cu(oaoH_2)_2(H_2O)]SO_4$ and $[Cu(oaoH_2)Cl_2]_n$ and listings of temperature factors and of calculated and observed structure amplitudes (27 pages). Ordering information is given on any current masthead page.

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Electron-Transfer Barriers and Metal–Ligand Bonding as a Function of Metal Oxidation State. 3. Crystal and Molecular Structures of Tris(2,2′-bipyridine)nickel(III) Triperchlorate–2-Acetonitrile–0.5-Dichloromethane[1,3]

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Received January 20, 1984

The structure of tris(2,2′-bipyridine)nickel(III) triperchlorate–2-acetonitrile–0.5-dichloromethane, $[Ni(C_{10}H_8N_2)_3](ClO_4)_3\cdot 2CH_3CN\cdot 0.5CH_2Cl_2$, has been determined. The nickel(III) complex crystallizes in the triclinic crystal system, space group $P\bar{1}$, with $a = 11.193$ (1) Å, $b = 17.634$ (3) Å, $c = 10.494$ (2) Å, $\alpha = 95.41$ (1)°, $\beta = 107.02$ (2)°, $\gamma = 95.28$ (1)°, and $Z = 2$. The structure was refined to a final R value of 0.096. The coordination sphere consists of the six nitrogen atoms of the three bipyridine ligands in a tetragonally distorted octahedral arrangement about the nickel. The six nickel–nitrogen bonds form three sets with two pairs of longer equatorial bonds, 2.022 (6) and 2.000 (5) Å, and a pair of shorter axial bonds, 1.924 (6) Å. The metal–ligand bond distances in $Ni(bpy)_3^{3+}$ and related complexes are rationalized in terms of their electronic configurations. The electron-transfer barrier for the $Ni(bpy)_3^{3+}$–$Ni(bpy)_3^{2+}$ exchange is related to the bond length differences in the two oxidation states and is compared with the barrier for electron transfer between other polypyridine complexes.

Introduction

Although a number of theories of electron-transfer reactions have been proposed, there is general agreement that the changes in nuclear configuration that occur when a molecule or ion is oxidized or reduced is an important factor in determining electron-transfer rates.[4] If the reactants are two metal complexes, then these configuration changes include changes in the metal–ligand and intraligand bond distances and angles, as well as changes in the orientations of the surrounding (polar) solvent molecules. The series of tris(bipyridine) (or tris(phenanthroline)) complexes provide excellent systems for testing these models, since, despite the formal similarity of the polypyridine couples, their measured exchange rates span 8 orders of magnitude.

In terms of a recent semiclassical model[4–6] the rate constant k for an electron-exchange reaction such as

$$M(bpy)_3^{2+} + M(bpy)_3^{3+} \rightleftharpoons M(bpy)_3^{3+} + M(bpy)_3^{2+} \qquad (1)$$

may be expressed as the product of a preequilibrium constant K_A, an effective nuclear frequency ν_n, and electronic and nuclear factors κ_{el} and κ_n, respectively:

$$k = K_A \nu_n \kappa_{el} \kappa_n \qquad (2)$$

The value of the preequilibrium constant depends upon the

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(1) Part 2 in this series is ref 3.

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