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Synthesis, Magnetism, Electron Paramagnetic Resonance Studies, X-Ray Molecular Structure, and Spectral Properties of μ_4-Oxo-hexa-μ-chloro-tetrakis[(3-quinuclidinone)copper(II)]

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Received November 23, 1976 AIC60849Y

The title compound, which has been characterized by a single-crystal x-ray diffraction study, is shown to be a μ_4-oxo-bridged cluster compound of the general type $[Cu_4OX_{10-n}L_n]^{n-4}$. It crystallizes as orange pinacoidal crystals in the centric, monoclinic space group $P2_1/c$ with a = 11.877 (4) Å, b = 19.106 (3) Å, c = 21.975 (5) Å, β = 122.28 (2)°, V = 4328 Å^3, and Z = 4. Single-crystal x-ray diffraction data, complete to 2θ = 50° (Mo Kα radiation), were collected on a Syntex $P2_1$ automatic diffractometer, and the structure was solved by a combination of Patterson, Fourier, and least-squares refinement techniques. Final discrepancy values of R = 6.9% and R_w = 7.0% were obtained for 4798 independent reflections and 304 adjustable parameters. The molecule consists of a central oxide ion coordinated tetrahedrally to four copper(II) ions; the copper(II) ions are bridged in pairs by six chloride ions which comprise a fairly regular octahedron around the central oxide ion, O(1). A total of four molecules of 3-quinuclidinone (3-quin) complete the trigonal-bipyramidal coordination sphere around each copper(II) ion. The Cu_4OCl_6(3-quin)$_4$ molecule does not have rigorous T_d symmetry nor does the central oxide ion occupy any special crystallographic symmetry site in the unit cell. Nevertheless, a nearly perfect tetrahedron of copper(II) ions is observed around O(1). Some pertinent interatomic distances and angles are Cu–O(1) = 1.915–1.925 Å (average 1.919 ± 0.005 Å), Cu–O(1)–Cu = 108.9–110.3° (average 109.5 ± 0.5°), Cu–Cu = 3.120–3.155 Å (average 3.134 ± 0.013 Å), O(1)–Cl = 2.932–2.956 Å (average 2.946 ± 0.009 Å), Cl–Cl = 4.093–4.232 Å (average 4.161 ± 0.044 Å), Cl–O(1)–Cl = 88.2–91.9° (average 90.0 ± 1.3°), N–Cu–Cl = 94.5–96.3° (average 95.3 ± 0.6°), and O(1)–Cu–Cl = 83.9–85.9° (average 84.8 ± 0.5°). The existence of two distinct types of axial–equatorial angles about each copper—namely, N–Cu–Cl and O(1)–Cu–Cl—is witness to the fact that each copper(II) ion is displaced (in the direction of the nitrogen atom of 3-quinuclidinone) approximately 0.2 Å out of the equatorial plane of the three coordinated chloride ions. Magnetic susceptibility measurements in the temperature range 302.9–1.27 K revealed a ferromagnetic interaction between the four metal ions of the cluster to temperatures of ca. 20 K; below 20 K, the values of μ_{eff} rapidly decreased with decreasing temperature. The magnetic susceptibility per copper ion was fit to a modified Heisenberg model which included, in addition to the usual g factor and intramolecular exchange integral, an intermolecular exchange parameter, $z'J'$. The computed "best fit" for these parameters was g = 2.178 ± 0.010 cm^{-1}, J = 47.34 ± 2.15 cm^{-1}, and $z'J'$ = −0.316 ± 0.018 cm^{-1}, respectively. The low-temperature EPR spectra of powdered samples of this compound confirmed the g value and the ferromagnetic nature of the intramolecular exchange coupling.

Introduction

Our research into the relationship between magnetic properties and molecular structure has recently concentrated on magnetic exchange interactions in multinuclear transition metal complexes. Of particular interest have been tetranuclear complexes of copper(II) which have the general stoichiometry $[Cu_4OX_{10-n}L_n]^{n-4}$ where X represents a chloride or bromide ion and L represents a Lewis base ligand. These complexes contain both μ_4-bridging oxygen and μ-bridging halogens between the copper ions.

The first account of such complexes was a preliminary report on $Cu_4OCl_6(Ph_3PO)_4$ and $[(CH_3)_4N]_4[Cu_4OCl_{10}]$ given by Bertrand and Kelley.[1] It was Lines, Ginsberg, Martin, and Sherwood[11] who reported the unusual magnetic properties of the compounds. They found that for $Cu_4OCl_6(Ph_3PO)_4$, μ_{eff} increased to a maximum at temperatures in the range 40–60 K; below these temperatures the values of μ_{eff} rapidly decreased. On the contrary, the values of μ_{eff} for $[(CH_3)_4N]_4[Cu_4OCl_{10}]$ steadily decrease with decreasing temperature.

To date, numerous other accounts of such compounds have been reported[2-10,12-17] but few detailed magnetic investigations have been reported. We have prepared a tetramer of formula Cu_4OCl_6(3-quin)$_4$ containing both stoichiometric and nonstoichiometric amounts of solvent. We have studied the magnetism, spectral properties, and electron paramagnetic resonance spectra of the stoichiometric toluene solvate and determined the crystal and molecular structure of the nonstoichiometric solvate.

Experimental Section

Preparation of Cu_4OCl_6(3-quin)$_4$. A 1.00-g sample of 3-quinuclidinone hydrochloride (6.2 mmol, used as received from Aldrich Chemical Co.) dissolved in 50 mL of dry, boiling methanol was mixed with 1.05 g of $CuCl_2\cdot 2H_2O$ (6.2 mmol) also dissolved in 50 mL of dry, boiling methanol. A solution composed of 0.50 g of sodium methoxide (9.3 mmol) in 50 mL of hot methanol was added dropwise to this mixture. The reaction mixture gradually darkened, and a brown-orange solid formed; heating was continued for ca. 15 min after addition of $NaOCH_3$. After cooling to ambient temperature, the product was collected by filtration, washed with methanol, and dried in vacuo over P_4O_{10} overnight.

Recrystallization of the crude product from warm benzene gave a benzene solvate, Cu_4OCl_6(3-quin)$_4\cdot 0.75C_6H_6$. Anal. Calcd for $Cu_4C_{32.5}H_{48.5}N_4O_5Cl_6$: Cu, 24.39; C, 37.46; H, 4.69; N, 5.38; Cl, 20.41. Found: Cu, 24.67; C, 37.29; H, 5.05; N, 5.30; Cl, 20.55.

Recrystallization of the crude product from warm toluene gave a toluene solvate, Cu_4OCl_6(3-quin)$_4\cdot 0.75CH_3C_6H_5$. Anal. Calcd for $Cu_4C_{33.25}H_{50}N_4O_5Cl_6$: Cu, 24.15; C, 37.94; H, 4.79; N, 5.32; Cl, 20.21. Found: Cu, 23.76; C, 37.47; H, 4.66; N, 5.20; Cl, 19.99.

Crystals large enough for use in the collection of x-ray diffraction data were not obtained readily by recrystallization from either benzene or toluene. A few sizable, well-formed crystals were obtained by recrystallization of the toluene solvate from a chloroform–ethyl acetate mixture, and one of these crystals was selected for use in the data collection. The solvent content of these crystals was difficult to determine crystallographically because of disorder; however, the structural parameters for Cu_4OCl_6(3-quin)$_4$ could be ascertained. The recrystallized products appeared brownish yellow by reflected light; microscopic examination showed them to be microcrystalline needles, yellow by transmitted light.

Collection and Treatment of X-Ray Diffraction Data. The crystal chosen for data collection was an abbreviated pinacoid, the growth of one of the faces having been inhibited by contact with the solvent vessel. Maximum crystal dimensions in three orthogonal directions were 0.50 mm × 0.33 mm × 0.18 mm. The unit cell was found to be monoclinic and room-temperature cell dimensions were obtained from a least-squares fit of 15 reflections, centered by the half-height technique on a Syntex $P2_1$ automated four-circle diffractometer.

Crystal data: $Cu_4C_{28}H_{44}N_4O_5Cl_6\cdot$solvent, a = 11.877 (4) Å, b = 19.106 (3) Å, c = 21.975 (5) Å, β = 122.28 (2)°, V = 4238 Å^3, Z

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$= 4$, d_{measd}(flotation in aqueous $CdCl_2$) $= 1.70$ (1) g cm^{-3}, d_{calcd}(for toluene solvate) $= 1.69$ g cm^{-3}, $\mu = 24.95$ cm^{-1}; space group $P2_1/c$ from systematic absences $h0l$ when $l = 2n + 1$ and $0k0$ when $k = 2n + 1$.

Intensity data with $4° \leq 2\theta \leq 50°$ were collected on the Syntex $P2_1$ diffractometer by the 2θ–θ mode using graphite-monochromatized Mo Kα radiation (λ 0.710 69 Å) and a variable scan rate (7.32–29.30°/min). The intensities of three reflections were monitored and no significant crystal deterioration was observed. Of the more than 8000 independent reflections measured, 4798 had intensities greater than $2\sigma(I)$ where the net intensity I and its estimated standard deviation were calculated from $I = S(P - B_1 - B_2)$ and $\sigma^2(I) = S(P + B_1 + B_2)$. Lorentz, polarization, and absorption corrections were applied. Transmission factors ($0.511 \leq TF \leq 0.754$) were calculated using a version of Busing's Fortran IV program ORABS, the accuracy of which was verified with the test data of Alcock.[28]

Determination and Refinement of the Structure. The scattering factors of Cromer and Waber[29] for neutral copper, chlorine, oxygen, nitrogen, and carbon were used without further correction. The function minimized during least-squares refinement processes was $\sum w(|F_o| - |F_c|)^2$, where $w = 1/\sigma^2$ and $\sigma^2 = \sigma^2(I) + (0.02I)^2$. Discrepancy factors are defined by $R = [\sum||F_o| - |F_c||/\sum|F_o|] \times 100$ (%) and $R_w = [\sum w(|F_o| - |F_c|)^2/\sum w|F_o|^2]^{1/2} \times 100$ (%). All calculations were carried out on the Xerox SIGMA9 computer at Texas Christian University. In addition to various locally written programs, Zalkin's FORDAP Fourier summation program, Okaya's block-diagonal least-squares and distance–angle programs, Ibers' NUCLS modification of the Busing–Martin–Levy ORFLS full-matrix least-squares program, and Johnson's ORTEP plotting program were used.

Atomic coordinates for the four independent copper atoms were deduced from a three-dimensional Patterson synthesis and were refined by least-squares techniques. The chlorine, oxygen, nitrogen, and carbon atoms were located by means of subsequent difference Fourier syntheses. Toward the completion of the structure determination ($R = 11\%$) not all the atoms indicated in the formula for the toluene solvate could be located in the difference maps. The oxygen atoms of three 3-quinuclidinone ligands show a twofold disorder. The quinuclidinone coordinated to Cu(3) exhibits an approximate 50% occupancy for the two oxygen sites. Carbon C(18) which is attached to oxygen O(6) also is disordered. The carbon occupies one site when the oxygen O(6) is present and another site, C(19), when the oxygen occupies the O(5) site. This mirror or partial rotational disorder probably is associated with solvent and packing interactions. Detailed interpretations of these interactions is complicated by the disorder of the solvent molecules in the large cavities between the complexes. During recrystallization toluene molecules have been partially or entirely replaced by chloroform, ethyl acetate, or fragments of its hydrolysis. Positions for the solvate atoms were obtained from difference Fourier maps and were 1.3–3.4 e Å^{-3} in magnitude. These peaks could not be associated with any particular model for a solvent molecule. Initially the coordinates and occupancy factors for these solvate atoms were refined employing fixed isotropic temperature factors ($B = 6.0$ Å^2) and carbon scattering factors, but toward the completion of least-squares refinement, the occupancy factors were fixed at their refined values and the temperature factors were allowed to vary. No attempt was made to locate hydrogen atoms.

Full-matrix and block-diagonal least-squares techniques were used in the final stages of refinement. Anisotropic temperature factors were applied to the central oxygen atom and the four copper and six chlorine atoms, and isotropic temperatures were applied to the remaining atoms. With 62 atoms (51 isotropic and 11 anisotropic), 304 parameters, and 4798 observables, the final discrepancy factors were $R = 6.9\%$ and $R_w = 7.0\%$, with a standard deviation of 0.865 for observations of unit weight.

Observed and calculated structure factors are available as supplementary material. Final atomic positional and isotropic thermal parameters are listed in Table I; anisotropic thermal parameters are given in Table II.

Physical Measurements. Magnetic susceptibility data in the temperature range ~300–~25 K were collected using a Faraday balance as previously described.[18] Magnetic susceptibility data at temperatures below 35 K were obtained by the Faraday method using a Cahn RG electrobalance and a Janis Varitemp cryostat. An SiO_2 sensor was used to measure temperatures above 30 K, a GaAs sensor was used for temperatures below 30 K, and the vapor pressure of helium was used to determine temperatures below 4.2 K. Temperature control was ±0.001 to ±0.01 K for temperatures greater than 4.2 K and ±0.001 K or better for lower temperatures.

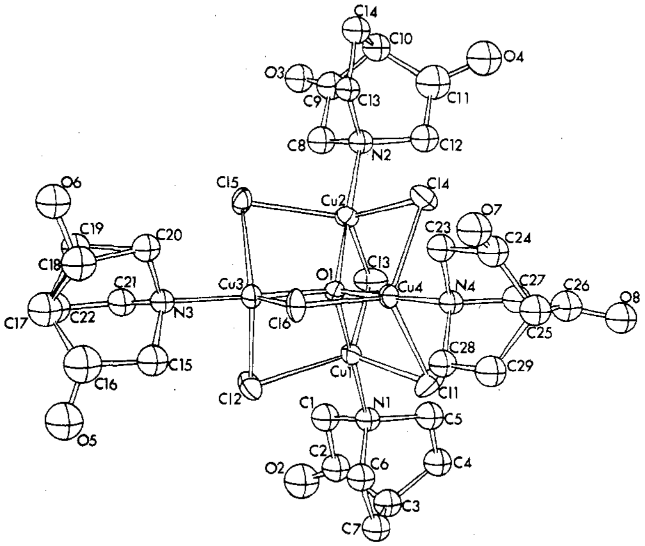

Figure 1. Overall stereochemistry of one molecule of $Cu_4OCl_6(3\text{-quin})_4$. The atoms O(3) and O(4), O(5) and O(6), O(7) and O(8), and C(18) and C(19) represent approximate twofold disordered positions in the three 3-quinuclidinone ligands.

Electron paramagnetic resonance studies were made using a basic ku-band homodyne spectrometer configuration with a low-noise back-diode detector system. The microwave source, a Varian X-12 klystron, was frequency-stabilized to the sample cavity to ensure sensitivity to the resonant absorption. A powdered, microcrystalline sample was packed into a spectroscopic grade quartz tube and inserted into the center of the spectrometer cavity turned to ca. 13.5 GHz for the TE_{102} mode. A reference sample of DPPH (2,2-diphenyl-1-picrylhydrazyl) was placed in the bottom of the cavity. A Varian V-3900 12-in. Mack I Fieldial magnet provided the resonant magnetic field as well as a linear scanning field with a precise x-axis output. A cryogenic Dewar system provided stable temperatures of 77 and 4.2 K. Precise laboratory g values were determined by simultaneously measuring the resonant microwave frequency and the resonant NMR frequency of a sample of H_2O at the EPR magnetic field. Both the NMR frequency and the EPR frequency were calibrated with reference to the same crystal-controlled time base. The EPR spectrometer was interfaced with a two-channel analog-to-digital convertor which allowed accurate numerical analysis of the line shape of the resonant absorption.

Electronic absorption spectra were obtained using a Cary 14 spectrophotometer by emulsifying the solid in a fluorocarbon grease and mounting the emulsion between two thin quartz plates; spectra of solutions were obtained using matched quartz cells. Infrared spectra in the range 4000–200 cm^{-1} were recorded on a Perkin-Elmer 621 spectrophotometer; the samples were prepared by grinding the copper complex with KBr or CsI and pressing the resulting powders into thin disks.

Elemental analyses were performed by Galbraith Laboratories, Inc., Knoxville, Tenn.

Results and Discussion

X-Ray Molecular Structure. The geometry of the $Cu_4OCl_6(3\text{-quin})_4$ molecule is shown in Figure 1 along with the labeling system used in the discussion. Interatomic distances, with their estimated standard deviations (esd's), are collected in Table III; bond angles, with esd's, are given in Table IV.

The molecule consists of a tetrahedron of copper(II) ions held together by one central μ_4-bridging oxide ion and six μ-bridging chloride ions; a 3-quinuclidinone molecule is bound to each copper ion via nitrogen in a terminal fashion. The Cu_4O tetrahedron is approximately regular, although perfect T_d symmetry is neither achieved nor required by crystallographic site symmetry; the central oxygen atom occupies a

Table I. Final Positional and Isotropic Thermal Parameters for $Cu_4OCl_6(3\text{-quin})_4 \cdot x(\text{solvate})$[a]

Atom	x	y	z	B, Å^2
Cu(1)	0.014 14 (11)	0.032 08 (6)	0.193 34 (6)	
Cu(2)	0.001 33 (11)	0.195 01 (6)	0.182 39 (6)	
Cu(3)	−0.161 76 (10)	0.114 92 (6)	0.236 34 (5)	
Cu(4)	0.149 25 (10)	0.122 66 (6)	0.333 41 (5)	
Cl(1)	0.219 27 (25)	0.014 24 (14)	0.308 33 (14)	
Cl(2)	−0.189 74 (27)	−0.000 74 (14)	0.185 71 (17)	
Cl(3)	0.014 94 (33)	0.107 15 (14)	0.106 37 (15)	
Cl(4)	0.197 78 (26)	0.229 23 (14)	0.292 89 (14)	
Cl(5)	−0.220 35 (23)	0.215 94 (14)	0.159 31 (14)	
Cl(6)	−0.013 87 (20)	0.122 53 (14)	0.365 86 (11)	
N(1)	0.028 9 (7)	−0.057 3 (4)	0.148 9 (4)	3.24 (14)
N(2)	0.002 7 (7)	0.277 9 (4)	0.125 6 (4)	3.35 (14)
N(3)	−0.330 6 (7)	0.114 1 (4)	0.238 5 (4)	3.30 (13)
N(4)	0.307 7 (7)	0.129 5 (4)	0.435 7 (4)	2.89 (13)
O(1)	0.000 2 (5)	0.116 2 (3)	0.236 2 (3)	
O(2)	−0.178 0 (10)	−0.164 1 (5)	−0.006 5 (5)	7.62 (22)
O(3)[b]	−0.208 1 (13)	0.340 6 (8)	−0.057 7 (7)	7.46 (31)
O(4)[c]	0.242 3 (41)	0.373 6 (23)	0.109 5 (22)	10.4 (11)
O(5)[d]	−0.484 4 (30)	−0.006 9 (15)	0.291 8 (15)	13.94 (78)
O(6)[e]	−0.512 5 (35)	0.235 9 (20)	0.269 7 (18)	11.79 (89)
O(7)[f]	0.407 0 (37)	0.231 5 (20)	0.590 6 (20)	6.90 (82)
O(8)[g]	0.664 2 (12)	0.117 2 (7)	0.525 7 (6)	6.81 (26)
O(9)	−0.574 1 (8)	0.375 5 (4)	0.475 0 (4)	6.10 (18)
O(10)	−0.427 7 (9)	0.305 5 (5)	0.425 4 (5)	6.89 (20)
O(11)	−0.374 0 (11)	0.453 1 (6)	0.452 4 (6)	7.92 (25)
C(1)	−0.090 3 (11)	−0.067 9 (6)	0.074 4 (6)	4.46 (21)
C(2)	−0.081 5 (11)	−0.138 5 (6)	0.046 3 (6)	4.80 (23)
C(3)	0.047 4 (11)	−0.175 9 (6)	0.094 0 (6)	5.09 (24)
C(4)	0.157 4 (12)	−0.125 7 (6)	0.106 9 (6)	5.52 (25)
C(5)	0.154 2 (11)	−0.058 1 (6)	0.146 6 (6)	4.50 (21)
C(6)	0.032 8 (10)	−0.118 4 (6)	0.193 4 (6)	4.33 (19)
C(7)	0.055 4 (12)	−0.189 6 (6)	0.166 1 (6)	5.29 (24)
C(8)	−0.112 6 (11)	0.272 7 (6)	0.048 8 (6)	4.48 (21)
C(9)	−0.110 8 (12)	0.336 2 (6)	0.006 8 (6)	5.12 (23)
C(10)	−0.001 2 (11)	0.385 9 (6)	0.051 0 (6)	5.21 (23)
C(11)	0.128 9 (14)	0.343 5 (8)	0.081 9 (7)	6.76 (31)
C(12)	0.130 5 (11)	0.280 7 (6)	0.126 5 (6)	4.41 (21)
C(13)	−0.118 (10)	0.345 4 (5)	0.157 5 (5)	3.93 (19)
C(14)	−0.012 1 (11)	0.410 6 (6)	0.114 9 (6)	4.73 (22)
C(15)	−0.324 8 (11)	0.054 4 (6)	0.285 2 (6)	4.57 (22)
C(16)	−0.452 2 (16)	0.056 0 (8)	0.287 8 (8)	7.62 (35)
C(17)	−0.546 6 (12)	0.111 8 (7)	0.241 6 (7)	5.90 (26)
C(18)[h]	−0.456 9 (34)	0.167 1 (19)	0.292 7 (20)	5.98 (76)
C(19)[i]	−0.479 3 (19)	0.181 2 (11)	0.260 3 (12)	4.11 (38)
C(20)	−0.345 9 (11)	0.180 9 (6)	0.267 5 (6)	4.64 (22)
C(21)	−0.449 9 (11)	0.102 8 (6)	0.163 2 (6)	4.62 (22)
C(22)	−0.579 9 (13)	0.101 1 (7)	0.164 5 (7)	6.41 (19)
C(23)	0.301 7 (10)	0.196 2 (5)	0.470 9 (5)	4.14 (20)
C(24)	0.425 7 (12)	0.202 2 (6)	0.549 2 (6)	5.34 (25)
C(25)	0.513 4 (11)	0.138 0 (6)	0.567 4 (6)	4.56 (22)
C(26)	0.552 3 (11)	0.131 7 (6)	0.513 7 (6)	4.97 (23)
C(27)	0.434 5 (10)	0.129 2 (5)	0.436 3 (5)	4.19 (20)
C(28)	0.309 8 (10)	0.068 3 (5)	0.479 7 (5)	3.78 (19)
C(29)	0.428 9 (12)	0.072 1 (6)	0.557 7 (6)	5.38 (25)
C(30)[j]	−0.527 8 (26)	0.385 2 (15)	0.333 1 (15)	8.02 (57)
C(31)[k]	−0.336 8 (23)	0.419 5 (13)	0.496 8 (12)	6.38 (45)
C(32)[l]	−0.416 5 (39)	0.374 7 (21)	0.479 9 (21)	7.55 (83)
C(33)[m]	−0.514 4 (31)	0.353 6 (18)	0.372 6 (18)	8.75 (76)
C(34)[n]	−0.496 6 (37)	0.402 1 (19)	0.432 3 (20)	7.25 (79)
C(35)[o]	−0.531 4 (32)	0.407 1 (17)	0.489 0 (18)	5.76 (70)
C(36)[p]	−0.583 1 (44)	0.353 3 (24)	0.447 8 (24)	6.67 (95)
C(37)[q]	−0.394 7 (39)	0.456 1 (21)	0.484 4 (22)	5.70 (78)

[a] All atoms are at full occupancy unless indicated otherwise. Atoms O(3) and O(4), O(5) and O(6), and O(7) and O(8) correspond to disordered positions for the quinuclidinone oxygens. Atoms C(30)–C(37) refer to the refined positions for the disordered solvent atoms. The solvent atoms, O(9), O(10), and O(11), were identified from difference Fourier maps as full-weighted oxygen atoms and they refined accordingly. The occupancy values for atoms indicated in this table are given in the following footnotes. [b] 0.703. [c] 0.297. [d] 0.584. [e] 0.416. [f] 0.284. [g] 0.752. [h] 0.416. [i] 0.584. [j] 0.632. [k] 0.667. [l] 0.414. [m] 0.549. [n] 0.426. [o] 0.389. [p] 0.313. [q] 0.361.

general position in the space group $P2_1/c$. The pertinent interatomic distances and angles are as follows: Cu–O(1) = 1.915–1.925 Å (average 1.919 ± 0.005 Å),[30] Cu–O(1)–Cu = 108.9–110.3° (average 109.5 ± 0.5°), Cu–Cu = 3.120–3.155 Å (average 3.134 ± 0.013 Å).

The six chloride ions comprise a fairly regular octahedron around the central oxygen atom, O(1), although the Cl–Cl distances and Cl–O(1)–Cl angles vary markedly: O(1)–Cl = 2.932–2.956 Å (average 2.946 ± 0.009 Å), Cl–Cl = 4.093–4.232 Å (average 4.161 ± 0.044 Å), Cl–O(1)–Cl = 88.2–91.9° (average 90.0 ± 1.3°). These variations, however, are not as large as those observed in the structures of $Cu_4OCl_6(py)_4$[17] (O–Cl = 2.92–2.96 Å, Cl–Cl = 3.93–4.41 Å, Cl–O–Cl = 84–98°) and $Cu_4OCl_6(2\text{-Mepy})_4 \cdot xH_2O$[8] (O–Cl

Table II. Anisotropic Thermal Parameters ($\times 10^4$) for $Cu_4OCl_6(3\text{-quin})_4 \cdot x(\text{solvate})$[a]

Atom	β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
Cu(1)	83.4 (13)	19.4 (3)	21.8 (4)	0.0 (5)	26.0 (6)	−1.3 (3)
Cu(2)	78.6 (12)	20.7 (3)	20.7 (4)	1.3 (5)	23.9 (6)	2.7 (3)
Cu(3)	60.7 (10)	24.3 (3)	21.6 (3)	0.0 (6)	21.6 (5)	0.7 (3)
Cu(4)	61.8 (10)	20.7 (3)	18.7 (3)	−0.3 (5)	16.2 (5)	−0.4 (3)
Cl(1)	95.2 (29)	30.7 (9)	28.2 (9)	18.4 (13)	12.9 (13)	−5.8 (7)
Cl(2)	112.7 (31)	29.3 (9)	52.6 (12)	−21.6 (14)	54.5 (17)	−17.4 (9)
Cl(3)	228.2 (47)	24.7 (8)	35.9 (10)	4.7 (16)	71.0 (19)	2.3 (8)
Cl(4)	100.5 (30)	31.3 (9)	27.6 (9)	−20.0 (13)	12.3 (13)	5.8 (7)
Cl(5)	78.1 (25)	32.3 (9)	32.3 (9)	13.1 (12)	29.4 (13)	13.3 (7)
Cl(6)	68.2 (22)	37.7 (9)	19.4 (7)	−0.1 (12)	20.6 (10)	−0.8 (7)
O(1)	68.7 (56)	20.3 (17)	19.2 (17)	2.7 (30)	21.2 (27)	2.8 (16)

[a] The anisotropic thermal parameter is defined as $\exp[-\beta_{11}h^2 - \beta_{22}k^2 - \beta_{33}l^2 - 2\beta_{12}hk - 2\beta_{13}hl - 2\beta_{23}kl]$.

= 2.281–3.03 Å, Cl–Cl = 3.83–4.55 Å), where inter- and intramolecular steric hindrances were postulated as causes for the distortions in the chloride octahedron. No comparisons of such distortions are possible in the clusters $Cu_4OCl_6(OPEt_3)_4$[16] and $Cu_4OCl_6(TPPO)_4$[1,2] where crystallographic C_3 and T_d symmetry requirements exist. Because of the bulkiness of the 3-quinuclidinone ligand, it is surprising that severe distortion of the polyhedra Cu_4OCl_6 does not occur; however, the disorder associated with the 3-quinuclidinone ligands may be associated with steric interactions via the solvent molecules. Potential intermolecular interactions are listed in Table V. Intermolecular hydrogen bonding between solvent atoms O(10) and O(11) (2.882 (15) Å) probably occurs, but intermolecular hydrogen bonding between solvent and cluster atoms cannot be substantiated with the closest contact being 3.702 (14) Å between O(10) and O(3).

The coordination of the four copper atoms is nearly trigonal bipyramidal, with the copper atom displaced out of the plane of the three coordinated chlorine atoms by about 0.2 Å in the direction of the nitrogen atom of 3-quinuclidinone. Least-squares planes and deviations of atoms from the planes are given in Table VI. The N–Cu–Cl angles range from 94.5 to 96.4° (average 95.3 ± 0.6°) and the O(1)–Cu–Cl angles range from 83.9 to 85.9° (average 84.8 ± 0.5°) while the Cl–Cu–Cl angles range from 115.5 to 122.2°.

Finally, we note that nearly all of the C–C, C–N, and C–O bond distances, save only a few (C(18)–O(6) and C(18)–C(20)), are within their accepted range of values. Since three of the four 3-quinuclidinone ligands show a twofold disorder of the keto oxygen atoms, bond lengths and angles in this portion of the ligand are expected to show larger variations.

Magnetic Susceptibility Studies. We have obtained magnetic susceptibility data at 100 temperatures between 302.9 and 1.27 K; measurements at three to ten different field strengths were made at each temperature and revealed no dependence upon applied field. Selected magnetic data are compiled in Table VII and the behavior of μ_{eff} as a function of temperature is illustrated in Figure 2.

The maximum in μ_{eff} indicates the same magnetic phenomenon as in the case of $Cu_4OCl_6(TPPO)_4$. Lines et al. did detailed treatments of their magnetic data on that complex using two approaches, the first involving an orbitally nondegenerate cluster of copper(II) ions and the second involving an orbitally degenerate cluster.

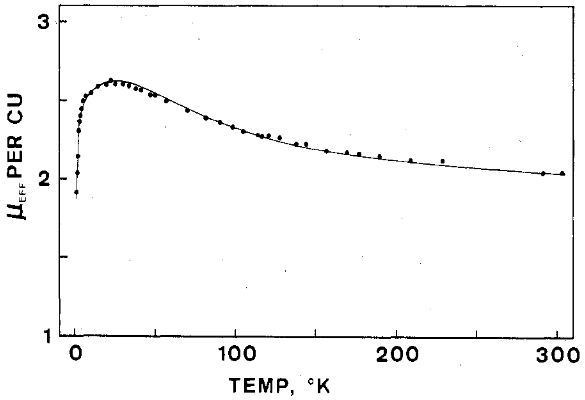

Figure 2. Variation of μ_{eff} per copper with temperature for $Cu_4OCl_6(3\text{-quin})_4 \cdot 0.75CH_3C_6H_5$: ●, experimental data; —, curve predicted by eq 4 with $g = 2.178$, $J = +47.34$ cm^{-1}, and $z'J' = -0.316$ cm^{-1}.

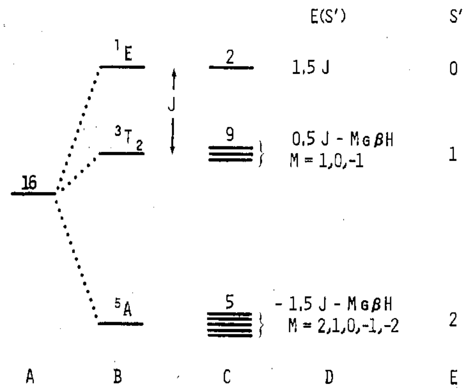

Figure 3. Energy level scheme for tetrahedron of weakly coupled spin $^1/_2$ ions: A, total degeneracy of the ground state for $J = 0$; *B*, symmetry labels describing system with $J \neq 0$; C, degeneracy with spin–spin coupling of form $-Js_i \cdot s_j$ and $J > 0$; D, relative energy of spin labels; E, sum of unpaired spin quantum number S'.

The first method is based upon the assumption that the magnetic properties may be explained by a simple Heisenberg exchange process, assuming an isotropic exchange interaction. Using the Hamiltonian

$$\mathcal{H} = -{}^1/_2 J(S^2 - 3) - g\mu_\beta H S^z \tag{1}$$

to describe the total spin of the tetramer, where *z* refers to the direction of the applied field, those authors calculated the spin energy level scheme as diagrammed in Figure 3. One derives a mathematical relationship between μ_{eff}, *T*, and the intramolecular exchange *J* by making calculations for the case where field strength approaches zero. Thus one finds

$$\mu_{eff}{}^2 = {}^3/_2 g^2 \mu_\beta{}^2 F(T) \tag{2}$$

where

$$F(T) = \frac{5 + 3\exp(-2J/kT)}{5 + 9\exp(-2J/kT) + 2\exp(-3J/kT)} \tag{3}$$

Using these relations and any given value of *J*, a graph of μ_{eff} vs. *T* does not exhibit a maximum. By allowing for a negative exchange (antiferromagnetic) between tetramers (intermolecular) which would dominate any high-temperature positive

Table III. Interatomic Distances (Å) for $Cu_4OCl_6(3\text{-quin})_4 \cdot x(\text{solvate})$

About Cu(1)	
Cu(1)-N(1)	2.021 (7)
-Cl(1)	2.421 (3)
-Cl(2)	2.419 (2)
-Cl(3)	2.394 (3)
-O(1)	1.915 (5)
About Cu(2)	
Cu(2)-N(2)	2.023 (7)
-Cl(3)	2.434 (3)
-Cl(4)	2.391 (3)
-Cl(5)	2.434 (1)
-O(1)	1.919 (5)
About Cu(3)	
Cu(3)-N(3)	2.032 (4)
-Cl(2)	2.416 (3)
-Cl(5)	2.412 (3)
-Cl(6)	2.422 (2)
-O(1)	1.925 (3)
About Cu(4)	
Cu(4)-N(4)	2.023 (6)
-Cl(1)	2.403 (3)
-Cl(4)	2.412 (3)
-Cl(6)	2.395 (1)
-O(1)	1.916 (5)
Interchlorine	
Cl(1)-Cl(2)	4.118 (3)
Cl(1)-Cl(3)	4.151 (4)
Cl(1)-Cl(4)	4.118 (4)
Cl(1)-Cl(6)	4.158 (3)
Cl(2)-Cl(5)	4.169 (4)
Cl(2)-Cl(6)	4.093 (4)
Cl(2)-Cl(3)	4.210 (3)
Cl(3)-Cl(4)	4.177 (4)
Cl(3)-Cl(5)	4.118 (3)
Cl(4)-Cl(5)	4.216 (3)
Cl(4)-Cl(6)	4.166 (3)
Cl(5)-Cl(6)	4.232 (3)
O(1)-chlorine	
O(1)-Cl(1)	2.946 (5)
-Cl(2)	2.940 (5)
-Cl(3)	2.956 (5)
-Cl(4)	2.932 (5)
-Cl(5)	2.935 (5)
-Cl(6)	2.944 (5)
quin 4	
N(4)-C(23)	1.512 (12)
N(4)-C(27)	1.498 (6)
N(4)-C(28)	1.510 (12)
C(23)-C(24)	1.561 (15)
C(24)-C(25)	1.517 (14)
C(25)-C(26)	1.485 (12)
C(26)-C(27)	1.519 (14)
C(28)-C(29)	1.535 (15)
C(29)-C(25)	1.552 (14)
C(24)-O(7)	1.186 (34)
C(26)-O(8)	1.240 (10)
Intercopper	
Cu(1)-Cu(2)	3.120 (2)
Cu(1)-Cu(3)	3.142 (1)
Cu(1)-Cu(4)	3.125 (1)
Cu(2)-Cu(3)	3.155 (1)
Cu(2)-Cu(4)	3.128 (1)
Cu(3)-Cu(4)	3.131 (1)
quin 1[a]	
N(1)-C(1)	1.499 (12)
N(1)-C(6)	1.509 (13)
N(1)-C(5)	1.515 (7)
C(1)-C(2)	1.510 (15)
C(2)-C(3)	1.497 (14)
C(3)-C(4)	1.521 (13)
C(4)-C(5)	1.571 (16)
C(6)-C(7)	1.566 (15)
C(7)-C(3)	1.559 (15)
C(2)-O(2)	1.215 (14)
quin 2	
N(2)-C(8)	1.505 (12)
N(2)-C(13)	1.520 (12)
N(2)-C(12)	1.508 (7)
C(8)-C(9)	1.531 (16)
C(9)-C(10)	1.479 (15)
C(10)-C(11)	1.544 (14)
C(11)-C(12)	1.542 (17)
C(13)-C(14)	1.557 (15)
C(14)-C(10)	1.552 (14)
C(9)-O(3)	1.265 (17)
C(11)-O(4)	1.281 (23)
quin 3	
N(3)-C(15)	1.511 (13)
N(3)-C(21)	1.513 (12)
N(3)-C(20)	1.481 (13)
C(15)-C(16)	1.545 (11)
C(16)-C(17)	1.486 (19)
C(17)-C(18)	1.495 (38)
C(17)-C(19)	1.488 (23)
C(18)-C(20)	1.701 (21)
C(19)-C(20)	1.505 (11)
C(21)-C(22)	1.559 (9)
C(22)-C(17)	1.536 (18)
C(16)-O(5)	1.279 (32)
C(18)-O(6)	1.435 (51)
C(19)-C(18)	0.670 (43)
Selected Distances within Solvate	
O(9)-C(34)	1.70 (3)
O(10)-C(32)	1.74 (4)
O(10)-C(33)	1.40 (3)
C(31)-C(32)	1.18 (4)
C(31)-C(34)	1.69 (4)
C(32)-C(37)	1.57 (6)
C(33)-C(34)	1.53 (5)
C(34)-O(11)	1.61 (3)
C(34)-C(35)	1.51 (4)
C(34)-C(36)	1.56 (4)
C(34)-C(37)	1.54 (5)
C(35)-C(36)	1.29 (6)

[a] quin 1 refers to the distances within the quinuclidinone ligand attached to Cu(1); similarly for quin 2, etc.

Table IV. Selected Interatomic Angles (deg) for $Cu_4OCl_6(3\text{-quin})_4 \cdot x(\text{solvate})$

About Cu(1)	
Cl(1)-Cu(1)-Cl(2)	116.6 (1)
Cl(1)-Cu(1)-Cl(3)	119.1 (1)
Cl(2)-Cu(1)-Cl(3)	122.1 (1)
N(1)-Cu(1)-Cl(1)	95.0 (2)
N(1)-Cu(1)-Cl(2)	95.2 (1)
N(1)-Cu(1)-Cl(3)	94.7 (2)
O(1)-Cu(1)-Cl(1)	84.7 (2)
O(1)-Cu(1)-Cl(2)	84.6 (1)
O(1)-Cu(1)-Cl(3)	85.9 (2)
O(1)-Cu(1)-N(1)	179.5 (2)
About Cu(2)	
Cl(3)-Cu(2)-Cl(4)	119.9 (1)
Cl(3)-Cu(2)-Cl(5)	115.5 (1)
Cl(4)-Cu(2)-Cl(5)	121.8 (1)
N(2)-Cu(2)-Cl(3)	95.2 (2)
N(2)-Cu(2)-Cl(4)	95.0 (2)
N(2)-Cu(2)-Cl(5)	96.2 (1)
O(1)-Cu(2)-Cl(3)	84.7 (2)
O(1)-Cu(2)-Cl(4)	85.0 (2)
O(1)-Cu(2)-Cl(5)	83.9 (1)
O(1)-Cu(2)-N(2)	179.9 (2)
About Cu(3)	
Cl(2)-Cu(3)-Cl(5)	119.4 (1)
Cl(2)-Cu(3)-Cl(6)	115.5 (1)
Cl(5)-Cu(3)-Cl(6)	122.2 (1)
N(3)-Cu(3)-Cl(2)	96.3 (2)
N(3)-Cu(3)-Cl(5)	96.0 (2)
N(3)-Cu(3)-Cl(6)	94.5 (2)
O(1)-Cu(3)-Cl(2)	84.5 (2)
O(1)-Cu(3)-Cl(5)	84.4 (2)
O(1)-Cu(3)-Cl(6)	84.4 (2)
O(1)-Cu(3)-N(3)	178.9 (2)
About Cu(4)	
Cl(1)-Cu(4)-Cl(4)	117.6 (1)
Cl(1)-Cu(4)-Cl(6)	120.1 (1)
Cl(4)-Cu(4)-Cl(6)	120.0 (1)
N(4)-Cu(4)-Cl(1)	94.6 (2)
N(4)-Cu(4)-Cl(4)	95.2 (1)
N(4)-Cu(4)-Cl(6)	95.2 (2)
O(1)-Cu(4)-Cl(1)	85.2 (1)
O(1)-Cu(4)-Cl(4)	84.4 (2)
O(1)-Cu(4)-Cl(6)	85.3 (1)
O(1)-Cu(4)-N(4)	179.5 (2)
About O(1)	
(1) Octahedron of Cl Atoms	
Cl(1)-O(1)-Cl(2)	88.8 (2)
Cl(1)-O(1)-Cl(4)	89.0 (1)
Cl(2)-O(1)-Cl(5)	90.4 (1)
Cl(4)-O(1)-Cl(5)	91.9 (2)
Cl(6)-O(1)-Cl(1)	89.8 (2)
Cl(6)-O(1)-Cl(2)	88.2 (1)
Cl(6)-O(1)-Cl(4)	90.3 (2)
Cl(6)-O(1)-Cl(5)	92.1 (1)
Cl(3)-O(1)-Cl(1)	89.4 (1)
Cl(3)-O(1)-Cl(2)	91.1 (2)
Cl(3)-O(1)-Cl(4)	90.4 (1)
Cl(3)-O(1)-Cl(5)	88.7 (2)
(2) Tetrahedron of Cu Atoms	
Cu(1)-O(1)-Cu(2)	108.9 (2)
Cu(1)-O(1)-Cu(3)	109.8 (2)
Cu(1)-O(1)-Cu(4)	109.3 (2)
Cu(2)-O(1)-Cu(3)	110.3 (2)
Cu(2)-O(1)-Cu(4)	109.3 (2)
Cu(3)-O(1)-Cu(4)	109.2 (2)
Cu-Cl-Cu	
Cu(1)-Cl(1)-Cu(4)	80.76 (8)
Cu(1)-Cl(3)-Cu(2)	80.51 (9)
Cu(1)-Cl(2)-Cu(3)	81.05 (8)
Cu(2)-Cl(4)-Cu(4)	81.26 (8)
Cu(2)-Cl(5)-Cu(3)	81.24 (7)
Cu(3)-Cl(6)-Cu(4)	81.05 (6)
quin 1[a]	
C(1)-N(1)-C(5)	109.6 (6)
C(1)-N(1)-C(6)	106.6 (7)
C(5)-N(1)-C(6)	108.8 (6)
N(1)-C(1)-C(2)	109.7 (8)
C(1)-C(2)-C(3)	114.1 (9)
C(1)-C(2)-O(2)	120.9 (9)
C(3)-C(2)-O(2)	124.5 (11)
C(2)-C(3)-C(4)	106.5 (9)
C(2)-C(3)-C(7)	106.0 (7)
C(4)-C(3)-C(7)	109.7 (9)
C(3)-C(4)-C(5)	110.5 (6)
C(4)-C(5)-N(1)	110.0 (7)
N(1)-C(6)-C(7)	112.1 (7)
C(6)-C(7)-C(3)	108.3 (9)
quin 2	
C(8)-N(2)-C(12)	108.9 (6)
C(8)-N(2)-C(13)	108.3 (7)
C(12)-N(2)-C(13)	109.0 (6)
N(2)-C(8)-C(9)	109.0 (8)
C(8)-C(9)-C(10)	113.8 (9)
C(8)-C(9)-O(3)	115.4 (10)
C(10)-C(9)-O(3)	130.5 (12)
C(9)-C(10)-C(11)	105.9 (10)
C(9)-C(10)-C(14)	108.6 (7)
C(11)-C(10)-C(14)	107.9 (10)
C(10)-C(11)-C(12)	111.0 (7)
C(10)-C(11)-O(4)	121.6 (24)
C(12)-C(11)-O(4)	113.3 (23)
C(11)-C(12)-N(2)	110.4 (7)
N(2)-C(13)-C(14)	111.4 (7)
C(13)-C(14)-C(10)	109.1 (9)
quin 3	
C(15)-N(3)-C(20)	109.3 (7)
C(15)-N(3)-C(21)	108.2 (7)
C(20)-N(3)-C(21)	109.6 (7)
N(3)-C(15)-C(16)	108.6 (8)
C(15)-C(16)-C(17)	112.8 (10)
C(15)-C(16)-O(5)	108.6 (13)
C(17)-C(16)-O(5)	125.2 (15)
C(16)-C(17)-C(18)	91.1 (16)
C(16)-C(17)-C(19)	110.6 (11)
C(16)-C(17)-C(22)	108.2 (10)
C(18)-C(17)-C(22)	125.7 (17)
C(19)-C(17)-C(22)	101.9 (11)
C(17)-C(19)-C(20)	114.0 (12)
C(17)-C(18)-C(20)	103.3 (19)
C(17)-C(18)-O(6)	111.9 (25)
C(20)-C(18)-O(6)	91.9 (20)
C(19)-C(20)-N(3)	108.8 (10)
C(18)-C(20)-N(3)	107.5 (14)
N(3)-C(21)-C(22)	109.9 (8)
C(21)-C(22)-C(17)	110.1 (9)
quin 4	
C(24)-N(4)-C(28)	108.2 (6)
C(23)-N(4)-C(27)	108.7 (6)
C(27)-N(4)-C(28)	108.6 (6)
N(4)-C(23)-C(24)	110.6 (7)
C(23)-C(24)-C(25)	110.0 (9)
C(23)-C(24)-O(7)	115.2 (17)
C(25)-C(24)-O(7)	124.2 (12)
C(24)-C(25)-C(29)	108.5 (6)
C(24)-C(25)-C(26)	108.4 (9)
C(26)-C(25)-C(29)	106.1 (9)
C(25)-C(29)-C(28)	109.5 (9)
C(29)-C(28)-N(4)	111.7 (7)
N(4)-C(27)-C(26)	109.3 (7)
C(27)-C(26)-C(25)	113.6 (6)
C(27)-C(26)-O(8)	118.2 (9)
C(25)-C(26)-O(8)	127.0 (11)

[a] quin 1 refers to interatomic angles within the quinuclidinone ligand attached to Cu(1); similarly for quin 2, etc.

intramolecular exchange (i.e., ferromagnetic), the working equation[11] becomes

$$\mu_{\text{eff}}^2 = \frac{3g^2\mu_\beta^2 kT F(T)}{2kT - 4z'J'F(T)} \tag{4}$$

where the intermolecular exchange is defined by the empirical parameter $z'J'$. Thus, for given ferromagnetic J and antiferromagnetic $z'J'$, eq 4 yields a maximum in graphs of μ_{eff} vs. T.

The second approach used by Lines et al.[11] is based upon the assumption that the observed magnetic phenomenon (i.e.,

Table V. Selected Intermolecular Contacts (≤3.2 Å) in the Structure of $Cu_4OCl_6(3\text{-quin})_4 \cdot x$(solvate)

Atoms	Symmetry transformn on the 2nd atom[a]	Dist, Å
O(4)–C(29)	ii + v	3.159 (29)
O(8)–O(3)	ii + vii	3.046 (13)
C(9)–O(8)	ii + viii	3.049 (10)
O(10)–O(11)	i	2.882 (15)
C(18)–O(3)	ii	3.031 (37)
O(2)–O(7)	iv + vi	3.070 (34)
O(4)–O(7)	ii + v	2.984 (46)
C(35)–C(37)	iii + ix	2.914 (49)

[a] The Roman numerals refer to the transformation to be applied to the listed coordinate of the second atom: (i) x, y, z; (ii) $x, {}^1/_2 - y, {}^1/_2 + z$; (iii) $-x, -y, -z$; (iv) $-x, {}^1/_2 + y, {}^1/_2 - z$; (v) $x, y, z - 1$; (vi) $x, y - 1, z$; (vii) $x + 1, y, z$; (viii) $x - 1, y, z - 1$; (ix) $x - 1, y + 1, z + 1$.

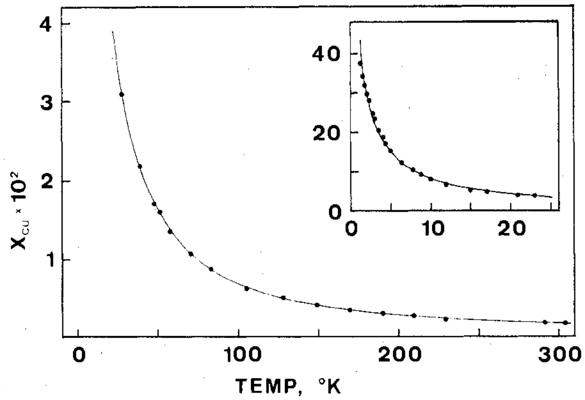

Figure 4. Variation of molar magnetic susceptibility per copper with temperature for $Cu_4OCl_6(3\text{-quin})_4 \cdot 0.75CH_3C_6H_5$: ●, experimental data; —, curve predicted by eq 4 with $g = 2.178$, $J = +47.34$ cm^{-1}, and $z'J' = -0.316$ cm^{-1}. The insert is a scaled-up version of the low-temperature region.

Table VI. Least-Squares Planes and Deviations (Å) of Atoms Therefrom[a,b]

Atom	Dev, Å	Atom	Dev, Å
A. Planes Defined by the Three Equatorial Cl Atoms about Each Cu Atom			
Equation (about Cu(1)): $-0.3416X + 0.8476Y + 0.4061Z = 2.9036$			
Cl(1)	0.0000	Cu(1)	−0.2075 (16)
Cl(2)	0.0000	N(1)	−2.228 (11)
Cl(3)	0.0000	O(1)	1.709 (9)
Equation (about Cu(2)): $0.3260X + 0.7850Y - 0.5267Z = 0.2171$			
Cl(3)	0.0000	Cu(2)	0.2303 (16)
Cl(4)	0.0000	N(2)	2.253 (11)
Cl(5)	0.0000	O(1)	−1.688 (8)
Equation (about Cu(3)): $-0.9999X - 0.0128Y + 0.0014Z = 4.4378$			
Cl(2)	0.0000	Cu(3)	0.2348 (15)
Cl(5)	0.0000	N(3)	2.266 (11)
Cl(6)	0.0000	O(1)	−1.690 (8)
Equation (about Cu(4)): $0.3346X + 0.0717Y + 0.9396Z = 5.0626$			
Cl(1)	0.0000	Cu(4)	0.2095 (15)
Cl(4)	0.0000	N(4)	2.232 (10)
Cl(6)	0.0000	O(1)	−1.707 (8)
B. Planes Defined by Four Atoms Comprising the Keto Groups on Each Quinuclidinone Ligand			
Equation (quin 1):[c] $-0.7367X - 0.4078Y + 0.5395Z = 2.698$			
C(1)	0.011 (16)	O(2)	0.016 (15)
C(2)	−0.041 (17)	C(3)	0.012 (18)
Equation (quin 2): $-0.8268X + 0.4922Y + 0.2723Z = 4.382$			
C(8)	0.008 (16)	O(3)	0.013 (21)
C(9)	−0.032 (18)	C(10)	0.011 (18)
Equation (quin 2): $-0.3399X + 0.4711Y + 0.8140Z = 4.373$			
C(10)	0.079 (18)	O(4)	0.105 (65)
C(11)	−0.236 (22)	C(12)	0.043 (15)
Equation (quin 3): $-0.1632X + 0.3680Y + 0.9154Z = 6.490$			
C(15)	−0.082 (17)	O(5)	−0.077 (43)
C(16)	0.226 (24)	C(17)	−0.072 (20)
Equation (quin 3): $0.009X - 0.2446Y + 0.9696Z = 3.9338$			
C(17)	−0.184 (20)	O(6)	−0.258 (54)
C(18)	0.481 (55)	C(20)	−0.023 (16)
Equation (quin 4): $-0.1134X + 0.4430Y + 0.8893Z = 10.833$			
C(23)	−1.171 (16)	O(7)	1.122 (57)
C(24)	0.110 (18)	C(25)	−0.226 (16)
Equation (quin 4): $0.1598X + 0.9868Y - 0.0257Z = 2.2582$			
C(25)	−0.017 (16)	O(8)	−0.025 (18)
C(26)	0.064 (17)	C(27)	−0.024 (15)

[a] Planes are in orthogonal (Å) Cartesian coordinates with X, Y, and Z axes in the direction of a^*, b, and $(a^* \times b)$, respectively. [b] Calculations were performed using the program DISTANG, by Y. Okaya. [c] quin 1 refers to plane calculations within the quinuclidinone ligand attached to Cu(1); similarly for quin 2, etc.

a maximum in μ_{eff} vs. T) is an intramolecular process. Their theory for the orbitally degenerate cluster is an elegant application of quantum mechanics which accounts for asymmetric exchange by three J values. Parameter J_1 involves major overlap in $\langle x^2 - y^2 | x'^2 - y'^2 \rangle$ by way of strong σ bonds on the same bridging halide ion; this coupling results in ferromagnetic behavior. The exchange parameter J_2 involves coupling through π bonding involving the μ_4-oxo bridge; this exchange is antiferromagnetic. Exchange defined by the J_3 parameter is a small contribution and is neglected to simplify the analysis. A significant feature of the degenerate orbital exchange treatment is the fact that it reduces to the simple Heisenberg model in cases where $J_1 + J_2 = J_1 - J_2$, that is, $J_2 = 0$.

In discussing the magnetic properties of the cluster $Cu_4OCl_6(py)_4$, Drake, Crawford, and Hatfield[17] have used nondegenerate theory and justified their treatment on the basis of previous studies by Hatfield and Piper[21] and Hatfield, Bedon, and Horner.[22] Those authors studied the trigonal-bipyramidal anion $CuCl_5^{3-}$, whose geometry is similar to that of the copper(II) ions in the tetranuclear clusters, and were led to conclude that the degenerate levels lie ca. 8000 cm^{-1} *above* the nondegenerate ground state.

Using a nonlinear least-squares curve-fitting computer program,[19] we fit 100 data points (all points equally weighted) for the compound reported here to eq 4. The values of the parameters g, J, and $z'J'$ were allowed to vary until sucessive iterations resulted in no significant change in their values. "Best fit" values were found to be $g = 2.178 \pm 0.010$, $J = 47.34 \pm 2.15$ cm^{-1}, and $z'J' = -0.316 \pm 0.018$ cm^{-1}. These values were used to obtain the solid curve in Figure 2. As can be seen in Figure 2, the agreement between experimental and calculated values is excellent, even at low temperatures.

In discussing the application of nondegenerate theory to their data for $Cu_4OCl_6(Ph_3PO)_4$, Lines et al.[11] were critical of the theory's inability to display the same susceptibilities found in their experiments. However, they did point out that corrections were made to their data to account for large paramagnetic

Table VII. Selected Magnetic Susceptibility Results for $Cu_4OCl_6(3\text{-quin})_4\cdot0.75CH_3C_6H_5$[a]

T, K	$10^{-6}\chi_M'$, cgsu	μ_{eff}, μ_B	T, K	$10^{-6}\chi_M'$, cgsu	μ_{eff}, μ_B
302.90	1 722	2.04	17.02	49 012	2.58
291.31	1 795	2.05	11.88	68 902	2.56
229.37	2 456	2.12	9.37	85 746	2.54
189.54	3 040	2.15	8.79	91 829	2.54
169.37	3 476	2.17	7.84	101 757	2.53
148.62	4 218	2.24	6.88	115 685	2.52
127.42	5 014	2.26	5.04	154 160	2.49
105.08	6 294	2.30	4.34	117 255	2.48
82.07	8 716	2.39	4.00	187 070	2.45
69.70	10 629	2.43	3.01	231 280	2.36
57.09	13 582	2.49	2.01	299 377	2.19
46.96	17 044	2.53	1.80	318 972	2.14
37.88	21 784	2.57	1.51	341 450	2.03
27.69	30 465	2.70	1.27	357 719	1.91
22.91	37 396	2.62			

[a] Values listed were calculated per copper; molar susceptibilities were corrected for diamagnetism using Pascal's constants; μ_{eff} was calculated using the relation $\mu_{eff} = 2.828(\chi_M'T)^{1/2}$. Calculated for $Cu_4OCl_6(3\text{-quin})_4\cdot0.75CH_3C_6H_5$: formula weight 1052.66; diamagnetic correction per mole of tetramer -570.0×10^{-6} cgsu.

impurities. In the case of $Cu_4OCl_6(3\text{-quin})_4\cdot0.75CH_3C_6H_5$, our ESR studies revealed no paramagnetic impurities. Figure 4 illustrates the variation of magnetic susceptibility with temperature. The predictions of the theory are in agreement with experiment at temperatures to 1.27 K. It would thus appear that the nondegenerate theory can in at least one case explain adequately the magnetic data for a Cu_4O cluster. It is also clear that the degenerate theory will give an equally good fit of the data if $J_2 = 0$. Although such a result is intuitively unsatisfactory, the possibility of other fits is not precluded and thus our results do not resolve the intermolecular vs. intramolecular question.

At present, we are continuing efforts to discover an experimental system which will allow us to confirm or refute dominant, antiferromagnetic tetramer–tetramer interactions at low temperatures. In so doing, it should be possible to demonstrate whether the maximum in μ_{eff} vs. T is due to intermolecular or intramolecular phenomena.

Electron Paramagnetic Resonance Studies. The EPR spectra of powdered samples[23] of the tetramer were consistent with the ground-state configuration predicted by the total effective spin Hamiltonian given by eq 1 with $J > 0$. No spectrum was observed at room temperature; however, a nearly symmetric resonant absorption was observed at 77 and 4.2 K. Taking the difference in the magnetic fields at the extremes in the derivative of the absorption spectrum as a measure of the line width, we found the width at 77 K to be 1700 G and at 4.2 K to be 600 G. Figure 5 illustrates an EPR spectrum for the tetramer taken at 4.2 K.

A noteworthy feature of the EPR spectra was that their intensities increased in going from 77 to 4.2 K in the same order as the absorption of the DPPH reference. This confirms that the ground-state manifold is paramagnetic and that the intracluster exchange interaction is primarily ferromagnetic; i.e., $J > 0$. In addition, no $\Delta M = \pm2$ transitions were observed and no hyperfine structure was evident except as a possible contribution to the inhomogeneous broadening of the line. A slight difference was found in the g values measured at 4.2 and 77 K. Taking the zero point in the resonance line as our laboratory g value, we determined g to be 2.164 ± 0.001 at 4.2 K and 2.160 ± 0.001 at 77 K; these values correspond to the "most likely" values of g. These values are in reasonable agreement with the value of 2.178 ± 0.010 obtained from the susceptibility data.

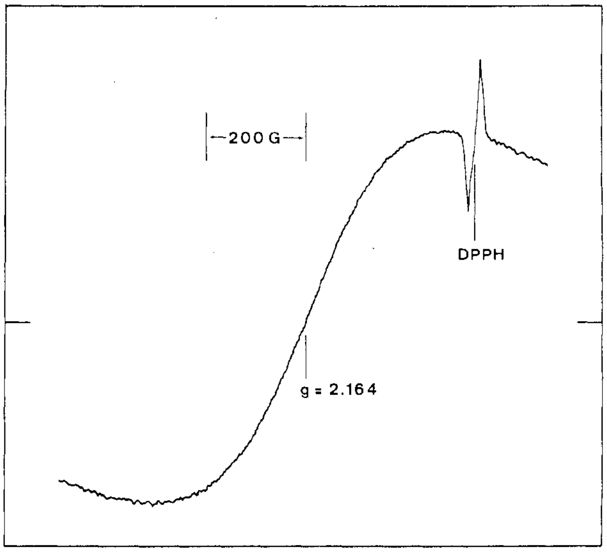

Figure 5. Central portion of the EPR spectrum of $Cu_4OCl_6(3\text{-quin})_4\cdot0.75CH_3C_6H_5$ at 4.2 K and 13.372 GHz.

The EPR spectrum at 4.2 K can be described by an abbreviated effective spin Hamiltonian for the ground-state manifold

$$\mathcal{H}_s = g\beta\bar{H}\cdot\bar{S}$$

with effective spin $S' = 2$ with only $\Delta m_s = \pm1$ transitions observed.

Essentially all of the intensity of the EPR spectrum at 4.2 K can be attributed to the ground-state manifold, whereas about 60% of the intensity of the EPR spectrum at 77 K was due to the excited triplet states at $J = \sim47$ cm^{-1}. Consequently, even though the EPR powder spectrum was broad, the agreement of the g values at 77 and 4.2 K indicates that the g factor of the excited-state manifold is essentially the same as that of the ground state.

Electronic Absorption Spectral and Infrared Spectral Results. We have observed the electronic absorption spectrum of $Cu_4OCl_6(3\text{-quin})_4\cdot0.75CH_3C_6H_5$ in the solid phase as an emulsion in fluorocarbon grease and in toluene solution. The spectrum of the complex in the solid phase consists of a broad, two-component band with peaks centered at ca. 11 430 and 12 900 cm^{-1} along with an absorption at ca. 25 640 cm^{-1} in the ultraviolet region. In toluene solution, the tetramer yields a spectrum of similar appearance with a broad, two-component band with peaks at ca. 11 430 and 12 900 cm^{-1} and an intense band at ca. 27 400 cm^{-1}. The molar extinction coefficients calculated per copper are large: ~385 for the peak at 11 430 cm^{-1}, ~315 for the peak at 12 900 cm^{-1}, and ~3200 for the ultraviolet band. The similarity between spectra obtained for different phases indicates that the clusters remain intact in solution. In fact, aged solutions showed no differences in their optical spectra.

Examination of the infrared spectrum of the cluster clearly showed the presence of the organic ligand 3-quinuclidinone. We located a broad band of medium intensity at ca. 568 cm^{-1} which we believe to be associated with the ν(Cu–O) frequency originating from vibrations in the Cu_4O core. In addition, another broad, medium-intensity band was found at ca. 225 cm^{-1} and is thought to be associated with the ν(Cu–Cl) frequency originating from the bridging chloride ions. Metal–halide stretching frequencies are known to occur in this range for halogen bridges between metals.[24] Support for these assignments was obtained by comparison of the infrared spectrum of the copper(II) chloride cluster with the spectrum of the analogous tetramer, $Cu_4OBr_6(3\text{-quin})_4$.[25] The spectra are essentially identical, except that for the bromide analogue, we find a broad, medium-intensity band at ca. 520 cm^{-1} which we assign to ν(Cu–O). No band down to energies of 200 cm^{-1} was found which could be assigned to the ν(Cu–Br) frequency. Its apparent shift to lower energy is consistent with vibrational differences between metal–chloride and metal–bromide bonds.

The general characteristics of $Cu_4OCl_6(3\text{-quin})_4\cdot 0.75CH_3C_6H_5$ compare with those found for other such systems: $CuCl_5^{3-}$ [22,26] and several tetramers.[1–17]

Acknowledgment. This research was supported by grants from the Robert A. Welch Foundation, Houston, Tex. (W.A.B.), and the National Science Foundation (W.H.W.). Both R.C.D. and F.T.H. held postdoctoral fellowships in chemistry from the Robert A. Welch Foundation, 1973–1976. We wish to thank Dr. John D. McNutt for supplying a copy of the nonlinear least-squares fitting program and for helping R.C.D to get the program running. Thanks are also extended to Dr. Bill Busing for supplying F.T.H. with the absorption correction program, ORABS. We greatly appreciate the help of Mr. Rizwan Mahmood in collecting the EPR data. Special thanks go to Dr. William R. Reiff (Northeastern University, Boston, Mass.) for obtaining the magnetism data below 25 K and to Professor J. Aaron Bertrand (Georgia Institute of Technology, Atlanta, Ga.) for giving F.T.H. the opportunity to use the Syntex $P2_1$ diffractometer.

Registry No. $Cu_4OCl_6(3\text{-quin})_4$, 62237-84-7.

Supplementary Material Available: Listing of structure factor amplitudes (22 pages). Ordering information is given on any current masthead page.

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Heavy-Metal Complexes of 2,4,6-Tris(2-pyrimidyl)-1,3,5-triazine. Structure of a Dilead Derivative

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Received December 28, 1976 AIC609189

The syntheses of four heavy-metal complexes of the ligand 2,4,6-tris(2-pyrimidyl)-1,3,5-triazine (TPymT) are reported. One of the complexes, 2,4,6-tris(2-pyrimidyl)-1,3,5-triazinedioxouranium(VI) nitrate heptahydrate, contains only one heavy-metal atom per ligand while the other three, bis[2,4,6-tris(2-pyrimidyl)-1,3,5-triazine]heptathallium(I) nitrate, 2,4,6-tris(2-pyrimidyl)-1,3,5-triazinetrilead(II) chloride trihydrate, and 2,4,6-tris(2-pyrimidyl)-1,3,5-triazinedilead(II) nitrate dihydrate, have more than one metal atom per ligand. The dilead complex crystallizes from aqueous solution as the dihydrate salt having the composition $C_{15}N_9H_9Pb_2(NO_3)_4\cdot 2H_2O$. The structure of this complex has been determined in a single-crystal x-ray diffraction study. The pale yellow complex crystallizes in the monoclinic space group $P2_1/n$ with four formula units per unit cell. The lattice parameters are $a = 14.192$ (2) Å, $b = 9.240$ (2) Å, $c = 19.621$ (3) Å, and $\beta = 90.173$ (6)°. By using 3184 independent observed reflections collected by diffractometer, the structure was solved and refined to a final discrepancy factor, R_1, of 0.044. The structure is twinned on the (100) plane. The proportion of each component of the twinned lattice was determined in the least-squares refinement. The twinning parameter refined to 0.160 (1) indicating the proportions of the two lattices to be 84:16. The triazine ligand binds two crystallographically unique lead atoms in two of its three tridentate sites. These lead atoms are bridged by the nitrate anion and water molecule oxygen atoms to form a polymer along the crystallographic *b* axis. The ring system of the 2,4,6-tris(2-pyrimidyl)-1,3,5-triazine ligand is puckered and a water molecule is hydrogen bonded in the third, terpyridine-like site. Conductivity data show the two lead atoms to remain coordinated to the TPymT ligand in aqueous solution.

Introduction

Interest in metals as probes of biological structure and function has grown during the last two decades. Metals have been used extensively as isomorphous replacement reagents for determining the phases of scattered x rays in crystal structures of macromolecules,[1] for probing the many parameters involved in the intercalative binding of drugs to deoxyribonucleic acid, DNA,[2–6] and for assessing site ac-