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Interpretation of Electronic and EPR Spectra of Copper(II) Amine Complexes: A Test of the MM−AOM Method

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The strain energy minimized structures (MM) of a series of copper(II) tetraamines ($[Cu((R)\text{-ahaz})((S)\text{-ahaz})]^{2+}$, (*R*)-ahaz (**1**) = (*R*)-3-aminohexahydroazepine, (*S*)-ahaz (**2**) = (*S*)-3-aminohexahydroazepine; $[Cu((S)\text{-ahaz})_2(OH_2)]^{2+}$; $[Cu(mn[13]aneN_4)(OH_2)_2]^{2+}$, mn[13]ane$N_4$ (**3**) = 12-methyl-12-nitro-1,4,7,10-tetraazacyclotridecane; $[Cu(mn[13]aneN_4)(OH_2)]^{2+}$; $[Cu(mn[14]aneN_4)(OH_2)]^{2+}$, mn[14]ane$N_4$ (**4**) = 6-methyl-6-nitro-1,4,8,11-tetraazacyclotetradecane; $[Cu(mn[15]aneN_4)(OH_2)]^{2+}$, mn[15]ane$N_4$ (**5**) = 10-methyl-10-nitro-1,4,8,12-tetraazacyclopentadecane; $[Cu(mn[15]aneN_4)(OH_2)_2]^{2+}$; $[Cu(mn[16]aneN_4)(OH_2)]^{+}$, mn[16]ane N_4 (**6**) = 3-methyl-3-nitro-1,5,9,13-tetraazacyclohexadecane; $[Cu(en)_2(OH_2)_2]^{2+}$, en (**7**) = ethane-1,2-diamine), with square planar, square pyramidal, and distorted octahedral chromophores exhibiting various degrees of tetrahedral distortion of the central coordination plane, are in good agreement with published X-ray structures (where available) and the two crystal structures reported in this paper. $[Cu(\mathbf{2})_2(ClO_4)](ClO_4)$ crystallizes in the orthorhombic space group $P2_12_12_1$, with a = 7.815(5) Å, b = 14.350(2) Å, c = 18.194(4) Å, Z = 4, and R_w = 0.061. $[Cu(\mathbf{5})(Cl)_2]\cdot 2H_2O$ crystallizes in the triclinic space group $P1$, with a = 6.884(2) Å, b = 9.090(3) Å, c = 9.214(2) Å, α = 105.13(2)°, β = 107.40(2)°, γ = 107.85(2)°, Z = 1, and R_w = 0.022. The spin Hamiltonian parameters and electronic transitions, estimated with the angular overlap model (AOM) based on the strain energy minimized structures of the chromophores, where generally water is used as axial ligand (MM−AOM), are in reasonable agreement with the calculated spectroscopic parameters based on experimental structures (AOM) and with the experimental spectroscopic data (UV−vis−near-IR and EPR spectra of single crystals, powders, glasses, and solutions). The calculated spectroscopic data are based on a constant set of electronic parameters which depend on the degree of substitution of the amine, on the Cu−N bond length, and on the degree of misdirected valences.

Introduction

The design of transition metal ion chromophores is an important and challenging task in areas such as bioinorganic chemistry (model compounds) and catalysis. Angular overlap model (AOM) calculations allow the computation of the electronic properties of transition metal complexes with some accuracy, provided the structure of the chromophore and the basic electronic parameters are known.[2] Molecular mechanics (MM) is a widely accepted method for a rather accurate calculation of structures, including those of transition metal complexes.[3,4] It then follows that a combination of both methods (MM−AOM), viz. AOM calculations based on structural parameters obtained via MM calculations, might be a viable method for the computational design of transition metal complexes with predetermined electronic properties. Clearly, this approach relies on constant and transferable sets of force field and electronic parameters. For molecular mechanics calculations this does not seem to be a problem, and we have recently developed force fields for a wide range of transition metal ions and ligand systems.[5] The AOM on the other hand has traditionally been used for the *interpretation* of electronic properties of metal complexes,[6] and transferability of the electronic parameters has been of lesser importance in that area.

The MM−AOM method has already been applied for Cr(III),[7] Co(III),[7] *low-spin* Fe(III),[8] and Ni(II)[7] complexes. Copper(II) is an essential and spectroscopically well-investigated metal ion in biological systems.[9−11] The Jahn−Teller active ground state leads to structural properties which are not *a priori* predictable by the classical molecular mechanics approach.[12] However, we recently have shown that for quasi tetragonal (4 + 2) and square pyramidal (4 + 1) geometries the positions of the central CuL_4 chromophore can be computed with the same precision as for other transition metal ion complexes, with the positions of the axial ligands being predicted with a somewhat inferior, but still acceptable, accuracy.[5] The aim of the present study was to test whether the calculated structures of the chromophores are sufficiently accurate for a meaningful prediction of the spectroscopic parameters of copper(II) complexes and to determine whether AOM calculations based on a single set of electronic parameters reproduce the observed spectroscopic data. We stress the following: (i) The MM approach used here does not *directly* include electronic effects.[3] Therefore, structure optimization of open-shell transition metal ion systems requires a well-tuned force field for each class of compounds. Our force field[5] has been carefully tested for many

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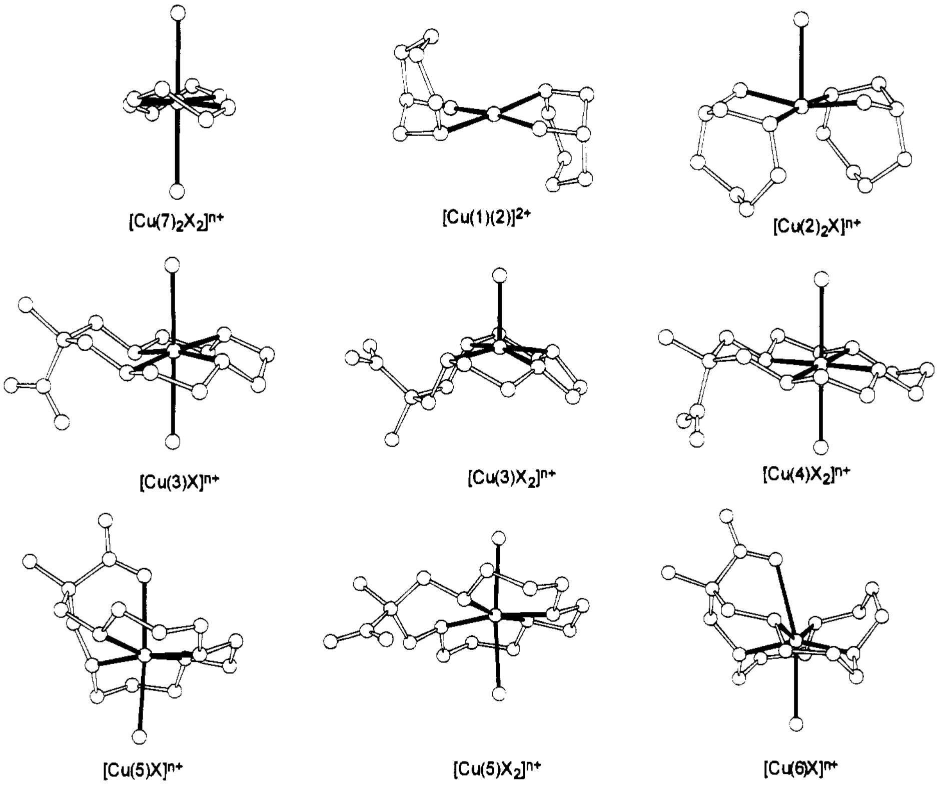

Figure 1. ORTEP[24] plots of the calculated (MM) structures of the chromophores of $[Cu(\mathbf{1})(\mathbf{2})]^{2+}$, **1** = (*R*)-ahaz = (*R*)-3-aminohexahydroazepine, **2** = (*S*)-ahaz = (*S*)-3-aminohexahydroazepine; $[Cu(\mathbf{2})_2(OH_2)]^{2+}$; $[Cu(\mathbf{3})(OH_2)_2]^{2+}$, **3** = mn[13]aneN$_4$ = 12-methyl-12-nitro-1,4,7,10-tetraazacyclotridecane; $[Cu(\mathbf{3})(OH_2)]^{2+}$; $[Cu(\mathbf{4})(OH_2)]^{2+}$, **4** = mn[14]aneN$_4$ = 6-methyl-6-nitro-1,4,8,11-tetraazacyclotetradecane; $[Cu(\mathbf{5})(OH_2)]^{2+}$, **5** = mn[15]aneN$_4$ = 10-methyl-10-nitro-1,4,8,12-tetraazacyclopentadecane; $[Cu(\mathbf{5})(OH_2)_2]^{2+}$; $[Cu(\mathbf{6})(OH_2)]^{+}$, **6** = mn[16]aneN$_4$ = 3-methyl-3-nitro-1,5,9,13-tetraazacyclohexadecane; $[Cu(\mathbf{7})_2(OH_2)_2]^{2+}$, **7** = en = ethane-1,2-diamine).

copper(II) complexes of the type discussed here.[3,5,13,14] (ii) Full transferability of ligand field parameters may not be warranted.[15-17] On the basis of (i) and (ii) some approximations are necessary in order to establish a simple tool for designing new compounds with given spectroscopic properties. Obviously, this will impinge on the accuracy of the results. Therefore, the aim of the present study was to investigate the accuracy and limitations of the MM−AOM method for tetragonally distorted copper(II) amines.

The complexes $[Cu(\mathbf{2})_2(ClO_4)]^+$ and $[Cu(\mathbf{1})(\mathbf{2})]^{2+}$ (see Figure 1) were chosen for the determination of the basic electronic parameters. These complexes are expected to provide a particularly good test for the extent to which AOM bonding parameters may be transferred from one compound to another, since (*R*)-ahaz (**1**) and (*S*)-ahaz (**2**) should have identical electronic properties but, due to the steric requirements of the ligand, the geometry of the chromophores of $[Cu(\mathbf{2})_2(ClO_4)]^+$ and $[Cu(\mathbf{1})(\mathbf{2})]^{2+}$ differ markedly. In complexes with saturated amines, π-interactions are unimportant. Therefore, in the absence of axial interactions such as in $[Cu(\mathbf{1})(\mathbf{2})]^{2+}$, the influence of ds-mixing on the energy of the d_{z^2} orbital can be deduced quantitatively. This also gives an important basis for the determination of a meaningful set of bonding parameters for axially coordinated solvent molecules or counterions such as in the pentacoordinate complex $[Cu(\mathbf{2})_2(ClO_4)]^+$. The parameters deduced from the two compounds were then tested and further refined in calculations of the copper(II) complexes of the macrocyclic tetraamine ligands **3**−**6** and $[Cu(\mathbf{7})_2(OH_2)_2]^{2+}$. The chromophores of the whole set include four-, five-, and six-coordinate copper(II), with various degrees of tetrahedral distortion of the CuN$_4$ core and primary as well as secondary amine ligands (see Figure 1).

Experimental Section

Materials. Optically pure and racemic 3-aminohexahydroazepine (**1** and **1**/**2**) were obtained from JPS Chimie, Bevaix, Switzerland, while 2,2,2-tet (1,8-diamino-3,6-diazaoctane), 2,3,2-tet (1,9-diamino-3,7-diazanonane), 3,2,3-tet (1,10-diamino-4,7-diazadecane), and 3,3,3-tet (1,11-diamino-4,8-diaazaundecane) were purchased from Fluka or Strem. $[Cu(\mathbf{1})(\mathbf{2})]^{2+}$,[18] $[Cu(\mathbf{2})_2]^{2+}$,[19] $[Cu(\mathbf{3})]^{2+}$,[20] $[Cu(\mathbf{4})]^{2+}$,[21] $[Cu(\mathbf{5})]^{2+}$,[22] and $[Cu(\mathbf{6})]^{2+}$ [22] were prepared via published methods (for structures and nomenclature of the copper(II) complexes, see Figure 1). The crystals of $[Cu(\mathbf{2})_2(ClO_4)]ClO_4$ and $[Cu(\mathbf{5})(Cl_2)]\cdot 2H_2O$ were obtained by slow evaporation of aqueous solutions of the corresponding salts.

Spectroscopy. EPR spectra were measured using either a JEOL JES-FE X-band, a Varian E15 Q-band (~10^{-4} M dmf/water (1:2), 77 K), or a Bruker ESP 300E spectrometer. Digitized UV−vis−near-IR single crystal spectra at temperatures between 10 and 298 K were

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Table 1. Crystal Data of [Cu((*S*)-ahaz)$_2$(ClO$_4$)]ClO$_4$ and [Cu(mn[15]ane)(Cl)$_2$]·2H$_2$O

	[Cu((*S*)-ahaz)$_2$(ClO$_4$)]ClO$_4$	[Cu(mn[15]ane)(Cl)2]·2H$_2$O
space group	$P2_12_12_1$	$P1$
a, Å	7.815(5)	6.884(2)
b, Å	14.350(2)	9.090(3)
c, Å	18.194(4)	9.214(2)
α, deg	90	105.13(2)
β, deg	90	107.40(2)
γ, deg	90	107.85(2)
V, Å^3	2040.4	482.66
fw	490.8	443.9
D_{calcd}, g cm^{-1}	1.600	1.527
empirical formula	$C_{12}H_{28}Cl_2CuN_4O_8$	$C_{12}H_{31}Cl_2CuN_5O_4$
Z	4	1
abs coeff, cm^{-1}	13.33	13.82
transm coeffs	0.922−0.814	0.840−0.636
temp, °C	21	21
λ	0.710 69	0.710 69
$R(F_\sigma)$	0.054	0.019
R_w	0.061	0.022

recorded on a microprocessor-controlled Cary 17 spectrophotometer fitted with a cryosystems LTS-21 standard universal closed-cycle refrigerator system and a Glan-Taylor polarizer or on a Varian Cary 2300 spectrophotometer fitted with a liquid nitrogen flow tube and a Glan-Taylor polarizer.

Calculations. MM calculations were performed with the molecular modeling package MOMEC,[23] which also produced ORTEP[24] files for plotting. The potential energy functions and the force field used have been described previously.[3,5] Starting coordinates were taken from crystal structures or produced with HyperChem.[25] AOM calculations were performed with a modified version of the computer program CAMMAG.[26,27]

X-ray Crystal Structure Determination. For both structures, cell constants were determined by a least-squares fit to the setting parameters of 25 independent reflections. Data were measured on an Enraf-Nonius CAD4-F diffractometer within the limit $2\theta_{max} = 50°$ with Mo Kα radiation, $\lambda = 0.710\ 69$ Å, graphite monochromator, and operation in the $\omega-1.33\theta$ scan mode. Data were reduced and Lorentz, polarization, and decomposition corrections were applied using the Enraf-Nonius Structure Determination Package (SDP).[28] The structures were solved by direct methods using the SHELXS-86 program[29] and were refined by full-matrix least-squares analysis with SHELX-76.[30] All non-hydrogen atoms were refined anisotropically. In the structure of [Cu(**2**)$_2$(ClO$_4$)]ClO$_4$ hydrogen atoms were included at calculated sites (C−H = 0.97 Å) with group temperature factors while *x*, *y*, *z*, and U_{iso} were refined for hydrogen atoms of [Cu(**5**)(Cl)$_2$]·2H$_2$O. Scattering factors not supplied by SHELX-76 were taken from the literature.[31] The crystal data are given in Table 1. Non-hydrogen atomic coordinates are listed in Tables 2 and 3, and the atomic nomenclature is defined in Figures 2 and 3. Listings of hydrogen atom coordinates and *U* values, anisotropic thermal parameters, and complete bond lengths, bond angles, torsion angles, and crystal data have been deposited as supporting information.

Table 2. Positional parameters (×10^4) for [Cu((*S*)-ahaz)$_2$(ClO$_4$)]ClO$_4$

	x	*y*	*z*	occ
Cu(1)	4873(2)	4237(1)	6094(1)	
N(1)	7083(14)	3902(9)	6596(6)	
N(2)	3777(14)	3515(8)	6932(6)	
N(3)	2718(14)	4697(7)	5667(6)	
N(4)	5934(14)	4741(7)	5151(6)	
C(1)	6742(25)	3566(14)	7316(8)	
C(2)	5129(27)	2999(8)	7300(6)	
C(3)	2520(43)	3941(23)	7341(19)	0.55(4)
C(4)	3309(61)	4455(36)	7951(24)	0.55(4)
C(5)	5289(44)	5033(20)	7720(16)	0.55(4)
C(6)	6696(38)	4462(17)	7843(12)	
C(7)	3068(22)	5294(11)	4973(8)	
C(8)	4578(21)	4813(10)	4611(7)	
C(9)	7223(25)	5434(13)	5213(11)	
C(10)	6642(33)	6336(19)	5174(14)	0.74(4)
C(11)	4933(42)	6536(15)	5592(12)	0.74(4)
C(12)	3460(53)	6393(26)	5112(21)	0.74(4)
C(3′)	2781(57)	4170(36)	7655(30)	0.45(4)
C(4′)	4152(54)	4987(28)	7863(20)	0.45(4)
C(5′)	5670(63)	4604(36)	8185(29)	0.45(4)
C(10′)	5852(56)	6533(24)	5431(21)	0.26(4)
C(11′)	3932(78)	6642(38)	5763(31)	0.26(4)
C(12′)	2768(52)	6212(29)	5144(21)	0.26(4)
C1(1)	4689(5)	1899(2)	5362(2)	
O(1)	6152(15)	1643(14)	5726(8)	
O(2)	3226(18)	1666(11)	5820(11)	
O(3)	4595(18)	1517(9)	4644(7)	
O(4)	4930(36)	2845(6)	5327(6)	
Cl(2)	5197(7)	3501(3)	1954(3)	
O(5)	5218(22)	4398(8)	1625(9)	
O(6)	5352(41)	2766(12)	1514(11)	
O(7)	4908(75)	3528(17)	2651(13)	
O(8)	6925(25)	3465(14)	2027(16)	
O(9)	299(55)	2804(24)	6527(19)	

Table 3. Positional parameters (×10^4) for [Cu(mn[15]ane)(Cl$_2$]·2H$_2$O

	x	*y*	*z*
Cu(1)	0	0	0
Cl(1)	3933(1)	1988(1)	140(1)
Cl(2)	−4078(1)	−2055(1)	−120(1)
N(1)	−1166(5)	1824(3)	408(4)
N(2)	−1498(4)	−743(3)	−2520(3)
N(3)	1003(4)	−1959(3)	−267(3)
N(4)	1553(4)	993(3)	2540(3)
C(1)	−1325(5)	2743(4)	−673(5)
C(2)	−2765(6)	1587(4)	−2443(5)
C(3)	−1687(6)	566(4)	−3181(4)
C(4)	−497(5)	−1643(4)	−3418(4)
C(5)	−793(4)	−3345(3)	−3392(3)
C(6)	−609(5)	−3496(3)	−1749(3)
C(7)	1495(5)	−2503(4)	1139(4)
C(8)	3043(6)	−1101(5)	2778(4)
C(9)	1943(6)	−50(5)	3456(4)
C(10)	443(6)	2015(5)	3186(4)
C(11)	53(6)	3000(4)	2158(4)
C(12)	822(6)	−3865(5)	−3998(5)
N(5)	−3205(4)	−4631(3)	−4582(3)
O(1)	−4679(4)	−4142(3)	−4770(3)
O(2)	−3537(5)	−6072(3)	−5223(4)
O(3)	6903(8)	6028(5)	2367(4)
O(4)	3714(8)	3886(5)	7610(5)

Results and Discussion

1. Crystal Structures. Structure of [Cu((*S*)-ahaz)$_2$(ClO$_4$)]ClO$_4$ (Cu(2)$_2$(ClO$_4$)]ClO$_4$). The structure of [Cu(**2**)$_2$(ClO$_4$)]ClO$_4$ consists of two diamines and a perchlorate ion coordinated to the copper(II) ion. The angle θ (see Chart 1) between the two planes defined by the two amine donors of each bidentate ligand and the copper(II) center (Cu(1)−N(1)−N(2) and Cu(1)−N(3)−N(4)) is 12.8° indicating a considerable tetrahedral

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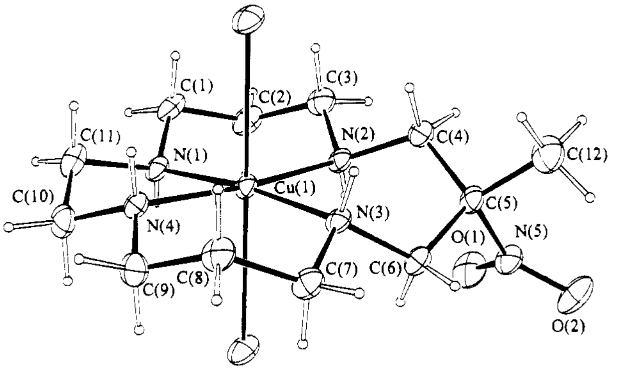


Figure 2. ORTEP[24] plot of the molecular structure of [Cu((S)-ahaz)$_2$-(ClO$_4$)]ClO$_4$, determined by X-ray crystallography.

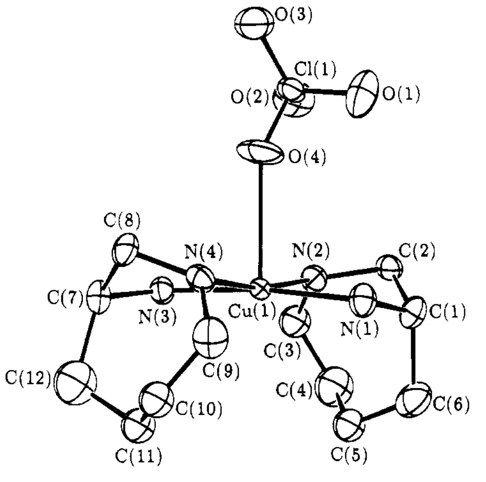
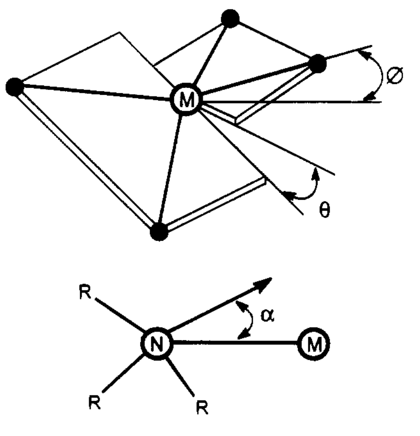


Figure 3. ORTEP[24] plot of the molecular structure of [Cu(mn[15]-aneN$_4$)(Cl)$_2$]·2H$_2$O, determined by X-ray crystallography.

Chart 1



distortion. The two secondary amines (N(2), N(4)) are oriented *trans* to each other and both have (R)-configurations, imposed by the stereogenic carbon atoms C(1) and C(7), respectively. The bond lengths and angles of the chromophore are given in Table 4. The Cu−N distances to the primary amines are somewhat shorter than the bond lengths to the secondary amines. The carbon atoms of the seven-membered 3-aminohexahydroazepine rings are disordered, but the chromophore is well resolved. The distance to the axial perchlorate (Cu(1)−O(4)) is 2.438 Å, and an uncoordinated perchlorate ion balances the charge. The axial bond to the perchlorate oxygen is, as expected, considerably shorter than the Cu−Br bond in structures of mixed bromide perchlorate salts [Cu(**2**)$_2$(Br)]$^+$ (Cu−Br ~ 2.8 Å).[18,19] All other structural features are similar to other structures of copper(II) complexes with ahaz.[18,19]

Table 4. Bond lengths (Å) and Angles (deg) for [Cu((S)-ahaz)$_2$(ClO$_4$)]ClO$_4$

N(1)−Cu(1)	2.012(10)	N(2)−Cu(1)	2.033(10)
N(3)−Cu(1)	1.968(10)	N(4)−Cu(1)	2.039(9)
O(4)−Cu(1)	2.438(8)	C(1)−N(1)	1.421(18)
C(2)−N(2)	1.454(18)	C(3)−N(2)	1.375(31)
C(3′)−N(2)	1.793(50)	C(7)−N(3)	1.551(16)
C(8)−N(4)	1.448(16)	C(9)−N(4)	1.421(18)
C(2)−C(1)	1.500(24)	C(6)−C(1)	1.605(26)
C(4)−C(3)	1.468(52)	C(5)−C(4)	1.806(54)
C(6)−C(5)	1.390(37)	C(5′)−C(6)	1.035(44)
C(8)−C(7)	1.517(21)	C(12)−C(7)	1.626(36)
C(12′)−C(7)	1.373(38)	C(10)−C(9)	1.375(28)
C(10′)−C(9)	1.948(45)	C(11)−C(10)	1.564(30)
C(12)−C(11)	1.459(39)	C(4′)−C(3′)	1.633(63)
C(5′)−C(4′)	1.433(56)	C(11′)−C(10′)	1.625(59)
C(12′)−C(11′)	1.574(67)	O(1)−Cl(1)	1.372(11)
O(2)−Cl(1)	1.455(17)	O(3)−Cl(1)	1.418(11)
O(4)−Cl(1)	1.371(9)	O(5)−Cl(1)	1.418(11)
O(6)−Cl(2)	1.330(18)	O(7)−Cl(2)	1.419(11)
O(8)−Cl(2)	1.358(19)		
N(2)−Cu(1)−N(1)	84.2(5)	N(3)−Cu(1)−N(1)	173.5(4)
N(3)−Cu(1)−N(2)	96.1(4)	N(4)−Cu(1)−N(1)	96.8(4)
N(4)−Cu(1)−N(2)	169.6(4)	N(4)−Cu(1)−N(3)	84.1(4)
O(4)−Cu(1)−N(1)	92.8(7)	O(4)−Cu(1)−N(2)	91.1(4)
O(4)−Cu(1)−N(3)	93.7(7)	O(4)−Cu(1)−N(4)	78.5(4)
C(1)−N(1)−Cu(1)	109(1)	C(2)−N(2)−Cu(1)	107.4(8)
C(3)−N(2)−Cu(1)	118(2)	C(3)−N(2)−C(2)	119(2)
C(3′)−N(2)−Cu(1)	117(2)	C(3′)−N(2)−C(2)	104(2)
C(7)−N(3)−Cu(1)	110.9(8)	C(8)−N(4)−Cu(1)	107.4(8)
C(9)−N(4)−Cu(1)	118(2)	C(9)−N(4)−C(8)	121(1)
C(2)−C(1)−N(1)	108(1)	C(6)−C(1)−N(1)	106(2)
C(6)−C(1)−C(2)	115(2)	C(1)−C(2)−N(2)	110(2)
C(4)−C(3)−N(2)	109(3)	C(5)−C(4)−C(3)	114(3)
C(6)−C(5)−C(4)	111(3)	C(5)−C(6)−C(1)	113(2)
C(5′)−C(6)−C(1)	122(4)	C(8)−C(7)−N(3)	103(2)
C(12)−C(7)−N(3)	116(2)	C(12)−C(7)−C(8)	111(2)
C(12′)−C(7)−N(3)	108(2)	C(7)−C(8)−N(4)	107(2)
C(10)−C(9)−N(4)	114(2)	C(10′)−C(9)−N(4)	101(2)
C(11)−C(10)−C(9)	115(3)	C(12)−C(11)−C(10)	111(3)
C(11)−C(12)−C(7)	112(3)	C(4′)−C(3′)−N(2)	105(3)
C(5′)−C(4′)−C(3′)	111(4)	C(4′)−C(5′)−C(6)	118(5)
C(11′)−C(10′)−C(9)	131(3)	C(12′)−C(11′)−C(10′)	103(3)
C(11′)−C(12′)−C(7)	116(3)	O(2)−Cl(1)−O(1)	108.4(8)
O(3)−Cl(1)−O(1)	112.6(9)	O(3)−Cl(1)−O(2)	113.4(8)
O(4)−Cl(1)−O(1)	100(2)	O(4)−Cl(1)−O(2)	111(1)
O(4)−Cl(1)−O(3)	110.3(8)	Cl(1)−O(4)−Cu(1)	141.4(7)
O(6)−Cl(2)−O(5)	117(1)	O(7)−Cl(2)−O(5)	112(2)
O(7)−Cl(2)−O(6)	129(2)	O(8)−Cl(2)−O(5)	93(1)
O(8)−Cl(2)−O(6)	86(2)	O(8)−Cl(2)−O(7)	94(3)

Crystal Structure of [Cu(mn[15]ane)(Cl)$_2$]·2H$_2$O ([Cu(5)-(Cl)$_2$]·2H$_2$O). The structure of [Cu(**5**)(Cl)$_2$] consists of the macrocyclic tetraamine and two chloride ions coordinated to copper(II), leading to a tetragonally distorted octahedral geometry. The configuration of the coordinated secondary amines is different from that of an earlier structure ([Cu(**5**)ClO$_4$]ClO$_4$), where the nitro substituent of the fused six-membered chelate ring was coordinated to the copper(II) center.[22] In the perchlorate structure the two amine centers N(2) and N(3) had different configurations allowing a boat conformation suitable for relatively unstrained bonding of the nitro group to the metal center. In the dichloride structure presented here both N(2) and N(3) have the same configuration leading to a skew boat conformation of the chelate ring involved. The other two six-membered chelate rings have chair conformations, and the five-membered ring has a δ conformation. The relevant bond lengths and angles are given in Table 5. The variation of Cu−N distances in the dichloride structure (2.05−2.08 Å) is smaller than in the perchlorate structure (2.00−2.09 Å), and the average Cu−N bond length is significantly larger for the dichloride structure (2.06 vs 2.04 Å). This is due to a smaller tetrahedral twist of the dichloride structure (6 vs 12°) enforced by the

Table 5. Bond Lengths (Å) and Angles (deg) for $[Cu(mn[15]ane)(Cl)_2]\cdot H_2O$

Cl(1)−Cu(1)	2.699(1)	Cl(2)−Cu(1)	2.806(1)
N(1)−Cu(1)	2.051(3)	N(2)−Cu(1)	2.058(3)
N(3)−Cu(1)	2.082(2)	N(4)−Cu(1)	2.060(3)
C(1)−N(1)	1.459(5)	C(11)−N(1)	1.479(4)
C(3)−N(2)	1.494(4)	C(4)−N(2)	1.471(4)
C(6)−N(3)	1.482(4)	C(7)−N(3)	1.488(4)
C(9)−N(4)	1.457(5)	C(10)−N(4)	1.489(4)
C(2)−C(1)	1.499(5)	C(3)−C(2)	1.507(5)
C(5)−C(4)	1.505(4)	C(6)−C(5)	1.527(4)
C(12)−C(5)	1.526(4)	N(5)−C(5)	1.542(3)
C(8)−C(7)	1.497(4)	C(9)−C(8)	1.513(5)
C(11)−C(10)	1.487(5)	O(1)−N(5)	1.212(4)
O(2)−N(5)	1.204(4)		

Cl(2)−Cu(1)−Cl(1)	179.6(0)	N(1)−Cu(1)−Cl(1)	95.9(1)
N(1)−Cu(1)−Cl(2)	84.0(1)	N(2)−Cu(1)−Cl(1)	91.5(1)
N(2)−Cu(1)−Cl(2)	88.9(1)	N(2)−Cu(1)−N(1)	92.4(1)
N(3)−Cu(1)−Cl(1)	89.3(1)	N(3)−Cu(1)−Cl(2)	90.7(1)
N(3)−Cu(1)−N(1)	173.7(1)	N(3)−Cu(1)−N(2)	91.0(1)
N(4)−Cu(1)−Cl(1)	85.7(1)	N(4)−Cu(1)−Cl(2)	93.9(1)
N(4)−Cu(1)−N(1)	82.7(1)	N(4)−Cu(1)−N(2)	174.1(1)
N(4)−Cu(1)−N(3)	94.2(1)	C(1)−N(1)−Cu(1)	119.7(2)
C(11)−N(1)−Cu(1)	109.9(2)	C(11)−N(1)−C(1)	110.5(3)
C(3)−N(2)−Cu(1)	117.7(2)	C(4)−N(2)−Cu(1)	114.0(2)
C(4)−N(2)−C(3)	106.5(2)	C(6)−N(3)−Cu(1)	113.4(2)
C(7)−N(3)−Cu(1)	117.1(2)	C(7)−N(3)−C(6)	106.1(2)
C(9)−N(4)−Cu(1)	121.4(2)	C(10)−N(4)−Cu(1)	108.2(2)
C(10)−N(4)−C(9)	111.5(3)	C(2)−C(1)−N(1)	111.7(3)
C(3)−C(2)−C(1)	113.0(3)	C(2)−C(3)−N(2)	114.2(3)
C(5)−C(4)−N(2)	116.8(2)	C(6)−C(5)−C(4)	115.2(2)
C(12)−C(5)−C(4)	108.4(3)	C(12)−C(5)−C(6)	112.5(3)
N(5)−C(5)−C(4)	109.3(2)	N(5)−C(5)−C(6)	102.7(2)
N(5)−C(5)−C(12)	108.4(2)	C(5)−C(6)−N(3)	114.8(2)
C(8)−C(7)−N(3)	114.3(3)	C(9)−C(8)−C(7)	113.3(3)
C(8)−C(9)−N(4)	111.2(3)	C(11)−C(10)−N(4)	107.9(3)
C(10)−C(11)−N(1)	108.1(3)	O(1)−N(5)−C(5)	117.9(2)
O(2)−N(5)−C(5)	118.5(3)	O(2)−N(5)−O(1)	123.6(3)

conformation of the chelate rings. The distance to the axial chloride ligands is rather long but in the expected range.

2. Molecular Mechanics Calculations. The structures of all nine chromophores discussed here (see Figure 1) have been modeled with MM. For generality, and to model the structures in solution, water molecules were used as axial ligands for the square pyramidal and octahedral geometries.[5] Except for $[Cu(\mathbf{3})(OH_2)]^{2+}$, where a full conformational analysis was performed due to a lack of relevant experimental data, only the experimentally observed geometries were refined. Relevant structural data of the MM structures are presented together with experimental parameters in Table 6.

A general problem of structure optimization of transition metal compounds is to model electronic effects exerted by the metal center. A prominent example is the Jahn−Teller effect, especially with copper(II) centers. Until recently, there was no general approach to solve this problem satisfactorily. We now have developed a rather simple algorithm that allows an accurate refinement of Jahn−Teller distorted systems with a general approach.[32] However, in copper(II) complexes such as those discussed here, the direction of the Jahn−Teller effect is predetermined by the ligand structure, i.e. in CuN_4X_n chromophores ($n = 1, 2$) the four amines define the equatorial plane while the additional ligands (OH_2 in aqueous solution, as described in our model systems) occupy the axial positions. Therefore, the simpler approach using distinct sets of k_{ML} and r_o for Cu−N, Cu−$O_{pentacoord}$, and Cu−$O_{hexacoord}$ (0.6, 0.1, 0.1 mdyn/Å; 1.970, 2.150, 2.500 Å, respectively) is sufficient.[5] A partly unsolved problem with this approach is that the coordination number may not be predicted. However, with species such as $[Cu(\mathbf{1})(\mathbf{2})]^{2+}$ and $[Cu(\mathbf{2})_2X]^{n+}$, where both or one axial sites, respectively, are blocked by the bulky backbone of the amine ligands (see Figure 1), and with $[Cu(\mathbf{3})X]^{n+}$, where the small size of the macrocyclic ligand forces the copper(II) center out of the plane defined by the four amine donors and therefore also blocks one of the axial sites (the hexacoordinate $[Cu(\mathbf{3})X_2]^{n+}$ complex is only stabilized in the crystal lattice), the geometry of the chromophore is basically predictable. Even with harmonic bonding potential functions, as they are used here, this leads to exceedingly large bond length and concomitantly to an increase in the strain energies in these structures.

In an evaluation of the accuracy of the calculated geometries it is important to remember that the environment is not considered *explicitly* in our MM calculations; i.e., the optimized structures represent "naked" molecules. However, the parametrization of the force field is based on crystal structural data, and environmental effects, averaged over the whole molecule, are therefore included in the parametrization. Thus, MM will refine in general to structures that are more symmetrical than observed in the crystal lattice, viz. specific distortions induced by crystal forces will be canceled, and it therefore is only reasonable to compare bond distances that are averages of symmetrically related parts of the undistorted model geometry. Obviously, with our aim to determine structures in solution and/or to design spectroscopic model compounds for bioinorganic systems this is not a severe restriction. On the basis of averaged geometric parameters, there is generally satisfactory agreement between calculated and experimental structures (see Table 6).

A discrepancy which is worthy of comment is the deviation from planar geometry of $[Cu(\mathbf{1})(\mathbf{2})]^{2+}$ by ca. 8°, compared to $\theta = 0°$ in the spectroscopically investigated diperchlorate salt and $\theta \sim 2.5°$ in the dibromide salt.[19] The two experimental structures suggest that some variation is expected due to crystal packing, but small inconsistencies in the force field parameterization, leading to an overestimation of θ in four-coordinate species, cannot be ruled out. A tetrahedral twist lowers all electronic energies, and indeed, a small but significant difference is observed between the solid state spectra of the diperchlorate and dibromide salts.[19] It is not possible to record meaningful solution spectra since $[Cu(\mathbf{1})(\mathbf{2})]^{2+}$ rearranges in solution to $[Cu(\mathbf{1})_2(OH_2)]^{2+}$ and $[Cu(\mathbf{2})_2(OH_2)]^{2+}$. Therefore, an experimental determination of the spectroscopic properties of the compound modeled via MM−AOM is not possible. From a comparison of the calculated electronic properties based on the X-ray and MM structures ($\theta = 0$ and 8°, respectively), it follows that the error due to the small tetrahedral twist might be appreciable.

$[Cu(\mathbf{3})(X)]^{n+}$ is the only other example where considerable discrepancy between the experimental and the optimized structure is observed. Here, it should be noted that the MM estimate of the axial distance, 2.195 Å, refers to a water molecule, whereas the axial ligand in the crystal structure is a chloride ion at 2.507 Å. The difference of ~0.31 Å is close to the difference between the covalent radii of oxygen and chlorine (0.3 Å), so that the calculated axial bond length agrees well with that observed experimentally.

3. Spectroscopy. The AOM parametrization is mainly derived from the analysis of the spectroscopic properties of $[Cu(\mathbf{1})(\mathbf{2})]^{2+}$ and $[Cu(\mathbf{2})_2(ClO_4)]^{+}$, based on single-crystal studies. While $[Cu(\mathbf{4})(ClO_4)_2]$ and $[Cu(\mathbf{5})(Cl)_2]$ have also been investigated as single crystals, the other compounds have been studied as powders or in solution. Spectroscopic data for $[Cu(\mathbf{7})_2(X)_2]$ were taken from the literature. We first discuss the assignments of the experimental data of $[Cu(\mathbf{1})(\mathbf{2})]^{2+}$ and $[Cu(\mathbf{2})_2(ClO_4)]^{+}$. A similar analysis was performed for the other two single-crystal studies. The data of all other compounds were treated in an

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(32) Comba, P.; Zimmer, M. *Inorg. Chem.* **1994**, *33*, 5368.

Table 6. Experimentally Determined and Calculated (MM) Structural Parameters for Cu(II) Tetrammines

compd	method[a]	Cu−N(1), Å	α for N(1), deg	Cu−N(2), Å	α for N(2), deg	Cu−N(3), Å	α for N(3), deg	Cu−N(4), Å	α for N(4), deg	Cu−X(1), Å	Cu−X(2), Å	θ, deg Cu(12), Cu(34)	θ, deg Cu(14), Cu(23)
$[Cu(\mathbf{7})_2X_2]^{n+}$	X-ray[b]	2.044		2.012		2.044		2.012		2.593	2.593		
	MM	2.005	3.1	2.005	3.1	2.005	3.1	2.005	3.1	2.522	2.522		
$[Cu(\mathbf{1})(\mathbf{2})]^{2+}$	X-ray[c]	1.979	1.0	2.036	8.0	1.979	1.0	2.036	8.0			0.0	0.0
	MM	1.994	3.7	2.035	7.1	1.996	4.0	2.037	7.3			8.6	7.9
$[Cu(\mathbf{2})_2X]^{n+}$	X-ray	2.012	0.2	2.033	15.7	1.969	0.9	2.038	16.4	2.437		12.8	11.7
	MM	2.014	4.5	2.013	8.7	2.014	4.5	2.013	8.7	2.317		15.1	14.0
$[Cu(\mathbf{3})X]^{n+}$	X-ray[d]	2.022	2.2	2.006	1.7	2.006	1.7	2.022	2.2	2.507		27.6	28.5
	MM	2.007	8.2	1.977	6.4	1.977	2.7	2.036	3.2	2.195		21.8	21.5
$[Cu(\mathbf{3})X_2]^{n+}$	X-ray[e]	1.943	1.8	1.959	7.3	1.959	7.3	1.943	1.8	2.620	2.650	6.1	6.2
	MM	1.968	4.3	1.964	4.9	1.985	5.8	1.968	1.3	2.707	2.546	12.4	12.4
$[Cu(\mathbf{4})X_2]^{n+}$	X-ray[f]	2.013	5.1	1.999	8.1	1.995	9.0	2.017	6.0	2.577	2.539	0.3	0.3
	MM	2.016	8.3	2.021	7.5	2.021	7.5	2.016	8.3	2.549	2.548	1.1	1.2
$[Cu(\mathbf{5})X]^{n+}$	X-ray[g]	2.005	12.4	2.033	9.1	2.016	10.3	2.093	12.0	2.443	2.580	11.0	11.9
	MM	2.017	12.9	2.044	7.9	2.026	8.9	2.065	13.7	2.453	2.533	16.6	17.9
$[Cu(\mathbf{5})X_2]^{n+}$	X-ray	2.082	7.7	2.060	11.9	2.051	11.0	2.058	9.3	2.806	2.699	6.1	6.4
	MM	2.069	7.0	2.064	9.2	2.067	9.5	2.071	6.7	2.548	2.571	12.4	13.1
$[Cu(\mathbf{6})X]^{n+}$	X-ray[h]	2.017	13.3	2.012	12.4	2.007	13.3	2.079	11.4	2.703	2.582	34.9	35.6
	MM	2.002	13.5	2.011	8.0	2.001	12.9	2.017	8.5	2.704	2.660	42.1	42.9

[a] OH_2 was used as an axial ligand for all MM calculations except for $[Cu(\mathbf{5})X]^{n+}$ and $[Cu(\mathbf{6})X]^{n+}$, where the pendent nitro group is coordinated. The axial ligands in the experimental structures were ClO_4, except for $[Cu(\mathbf{3})X]^{n+}$ and $[Cu(\mathbf{5})X_2]^{n+}$ (Cl) and for $[Cu(\mathbf{5})X]^{n+}$ and $[Cu(\mathbf{6})X]^{n+}$ ($X = R\text{-}NO_2$). [b] Komiyama, Y.; Lingafelter, E. C. *Acta Crystallogr.* **1964**, *17*, 1145. [c] Reference 18. [d] Reference 20. [e] Reference 20. [f] Reference 21. [g] Reference 22. [h] Reference 22.

Table 7. Experimentally Determined and Calculated (MM−AOM) Electronic Parameters for Cu(II) Tetraamines

compd	method[a]	$E_1(xy)$, cm^{-1}	$E_2(xz)$, cm^{-1}	$E_3(yz)$, cm^{-1}	$E_4(z^2)$ cm^{-1}	g_1	g_2	g_3	b, 10^3 cm^{-1}	A_1, 10^4 cm^{-1}	A_2, 10^4 cm^{-1}	A_3, 10^4 cm^{-1}
$[Cu(\mathbf{7})_2X_2]^{n+}$	exp[b]	19 700	19 700	17 900	14 100	2.06	2.06	2.17				
	AOM	21 100	18 980	19 500	15 790	2.04	2.05	2.17	52	17	39	200
	MM−AOM	20 430	19 080	19 870	13 310	2.04	2.04	2.16	6	26	29	205
$[Cu(\mathbf{1})(\mathbf{2})]^{2+}$	exp	22 210	22 210	22 210	19 880	2.04	2.06	2.14				
	AOM	21 630	20 180	21 080	20 180	2.04	2.04	2.15	6	27	30	207
	MM−AOM	20 160	18 730	19 620	18 680	2.04	2.04	2.17	10	25	30	202
$[Cu(\mathbf{2})_2X]^{n+}$	exp	19 300	19 300	19 300	16 430	2.05	2.05	2.16		31	31	200
	AOM	19 720	18 460	19 300	14 960	2.04	2.05	2.16	50	17	38	202
	MM−AOM	19 900	18 390	19 210	13 900	2.04	2.04	2.16	21	23	32	203
$[Cu(\mathbf{3})X]^{n+}$	exp	18 020	18 020	18 020	*c*							
	AOM	19 530	17 080	17 830	12 840	2.04	2.04	2.16	6	25	28	202
	MM−AOM	18 640	13 540	17 760	11 260	2.03	2.07	2.17	181	7	66	190
$[Cu(\mathbf{3})X_2]^{n+}$	exp	20 410	20 410	20 410	*c*							
	AOM	24 410	23 240	24 070	18 510	2.03	2.03	2.14				
	MM−AOM	23 250	22 100	23 020	17 200	2.04	2.04	2.14	10	27	32	212
$[Cu(\mathbf{4})X_2]^{n+}$	exp	20 830	20 400	20 800	*c*	2.05	2.05	2.15		35	35	199
	AOM	21 200	20 010	20 830	14 260	2.04	2.04	2.15	9	26	30	207
	MM−AOM	20 400	19 200	20 020	13 600	2.04	2.04	2.16	7	26	30	205
$[Cu(\mathbf{5})X]^{n+}$	exp	18 180	18 180	18 180	*c*							
	AOM	18 840	17 390	18 180	11 740	2.04	2.05	2.17	62	14	40	199
	MM−AOM	18 340	16 590	17 530	11 170	2.04	2.05	2.17	68	13	41	197
$[Cu(\mathbf{5})X_2]^{n+}$	exp	17 180	15 390	16 950	*c*	2.06	2.06	2.21		26	26	193
	AOM	17 480	16 210	17 020	10 720	2.05	2.05	2.21	17	22	30	194
	MM−AOM	17 320	16 010	16 820	11 130	2.05	2.05	2.19	7	24	28	194
$[Cu(\mathbf{6})X]^{n+}$	exp	17 240	16 130	16 130	*c*	2.06	2.06	2.21		23	23	184
	AOM	18 080	15 100	16 700	13 160	2.04	2.06	2.18	63	13	39	196
	MM−AOM	17 850	14 150	15 800	13 180	2.04	2.06	2.18	66	12	40	195

[a] OH_2 was used as an axial ligand for all MM calculations except for $[Cu(\mathbf{5})X]^{n+}$ and $[Cu(\mathbf{6})X]^{n+}$, where the pendent nitro group is coordinated. [b] Hathaway, B. J.; Stephens, F. *J. Chem. Soc. A* **1970**, 884. [c] Not resolved.

analogous manner. This is reasonable owing to the similarity of the chromophores and leads to a consistent overall analysis. The data are presented in Table 7.

Single-Crystal Electronic Spectra of $[Cu(\mathbf{1})(\mathbf{2})]^{2+}$ and $[Cu(\mathbf{2})_2(ClO_4)]^+$. The electronic spectra of $[Cu(\mathbf{1})(\mathbf{2})]^{2+}$ and $[Cu(\mathbf{2})_2(ClO_4)]^+$, recorded at 15 K with the electric vector along the two extinction directions of arbitrary crystal faces, are shown in Figure 4. The spectrum of $[Cu(\mathbf{1})(\mathbf{2})]^{2+}$ consists of two peaks, with Gaussian analysis of the more intense polarization suggesting that these are centered at 19 878 and 22 217 cm^{-1}. The complex is centrosymmetric, so that the intensity of the dd-transitions is derived solely from vibronic coupling. The ligand donor atoms approximate quite closely D_{4h} symmetry, and the only transition to be vibronically forbidden in this point group is $^2B_{1g}(d_{x^2-y^2}) \rightarrow {}^2B_{2g}(d_{xy})$ in z polarization. The higher energy band is somewhat weaker in one polarization than in the other (see Figure 4), suggesting that the $^2B_{1g}(d_{x^2-y^2}) \rightarrow {}^2B_{2g}(d_{xy})$ transition probably contributes to this. In a planar complex involving aliphatic amines, for which π-bonding contributions should be negligible, the $^2B_{1g}(d_{x^2-y^2}) \rightarrow {}^2E_g(d_{xz},d_{yz})$ transition should occur at this energy, so that the band at 19 878 cm^{-1} is due to the transition $^2B_{1g}(d_{x^2-y^2}) \rightarrow {}^2A_{1g}(d_{z^2})$. The assignment of the d_{z^2} transition of the square planar complex $[Cu(\mathbf{1})(\mathbf{2})]^{2+}$ is of importance to allow an accurate determination of e_{ds} (see

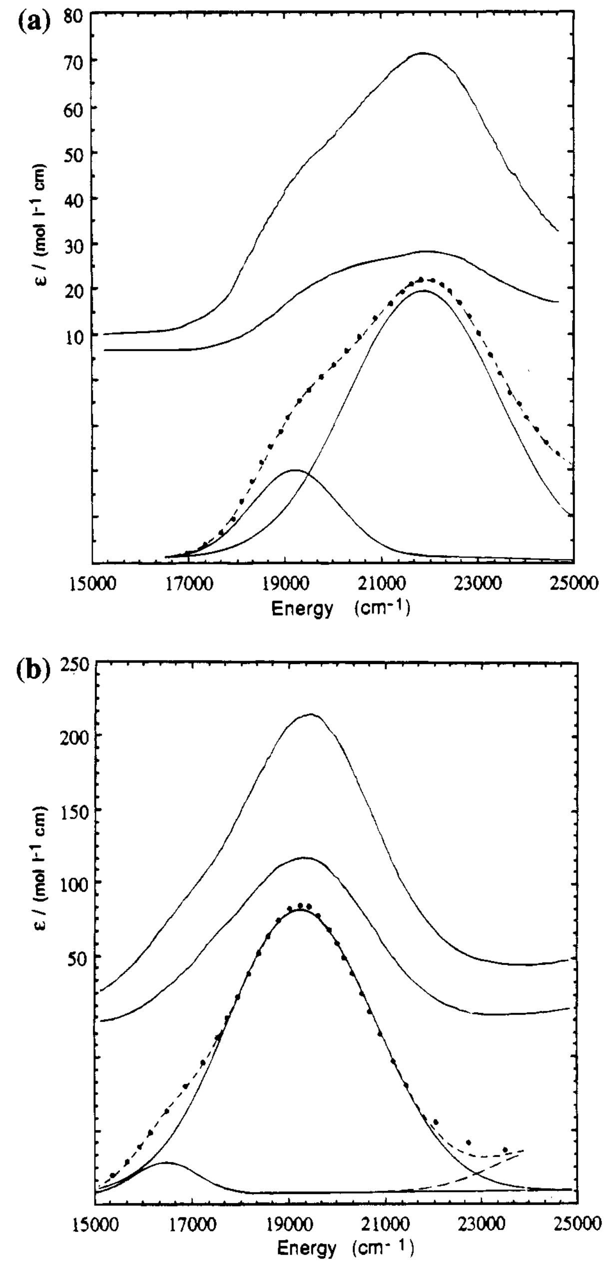

Figure 4. Electronic spectra of arbitrary crystal faces of (a) [Cu((*R*)-ahaz)((*S*)-ahaz)](ClO$_4$)$_2$ ([Cu(**1**)(**2**)](ClO$_4$)$_2$) and (b) [Cu((*S*)-ahaz)$_2$-(ClO$_4$)](ClO$_4$) ([Cu(**2**)$_2$(ClO$_4$)](ClO$_4$)) at 15 K with the electric vector along the two extinction directions (Gaussian fits included as dotted lines).

following section). The transition energy of this complex at 22 217 cm^{-1} is rather high and responsible for the unusual orange color of [Cu(**1**)(**2**)]$^{2+}$. This is expected since the separation between the d$_{xz}$, d$_{yz}$, and d$_{xy}$ set of orbitals and the partly empty d$_{x^2-y^2}$ orbital is at a maximum for square planar geometry and also because the proposed inverse correlation between equatorial and axial bonds in tetragonal copper(II) complexes[33,34] leads to a particularly high ligand field.

The spectrum of the complex [Cu(**2**)$_2$(ClO$_4$)]$^+$ also consists of two peaks, and in this case the interaction of the weakly bound perchlorate should act to lower the energy of the $^2B_{1g}(d_{x^2-y^2}) \rightarrow {}^2A_1(d_{z^2})$ transition, so that the lower energy band may confidently be assigned to this transition, with the $^2B_{1g}(d_{x^2-y^2}) \rightarrow {}^2B_2(d_{xy})$, $^2E(d_{xz},d_{yz})$ transitions both contributing to the higher energy band (the formal symmetry of the ligand coordination geometry in this complex is very low (see Tables 4 and 6), and for the sake of simplicity, symmetry labels appropriate to the D_4 point group have been used to specify the electronic states). As expected from the noncentrosymmetric nature of the complex, the bands are considerably higher in intensity than those in the planar complex (see Figure 4). The assignment of the transitions of all other compounds have been made in analogy (see Table 7) and are also consistent with the results from the AOM calculations (see below).

EPR Spectra of [Cu(1)(2)]$^{2+}$ and [Cu(2)$_2$(ClO$_4$)]$^+$. The experimentally determined EPR parameters of [Cu(**1**)(**2**)]$^{2+}$ and [Cu(**2**)$_2$(ClO$_4$)]$^+$ are also presented in Table 7. Due to line broadening caused by the anisotropy of the *g* factors and hyperfine interactions and by the interaction of the copper(II) centers with neighboring spins, no hyperfine splitting was resolved in the undiluted powder samples. In addition, the fast equilibrium between [Cu(**1**)(**2**)]$^{2+}$ and [Cu(**1**)$_2$(OH$_2$)]$^{2+}$/[Cu(**2**)$_2$(OH$_2$)]$^{2+}$ prevented recording of a frozen solution spectrum of [Cu(**1**)(**2**)]$^{2+}$.

The molecular *g* values and hyperfine constants may be related to the electronic transitions, and the relevant relations for d$_{x^2-y^2}$ ground states are given in eqs 1−4.[35] Here, $\Delta g_{x,y,z}$

$$\Delta g_z = \frac{-8k_z^{\,2}\lambda}{E_{xy}} \tag{1}$$

$$\Delta g_{x,y} = \frac{-2k_{xy}^{\,2}\lambda}{E_{xz,yz}} \tag{2}$$

$$A_z = P(-K\alpha^2 - {}^4/_7\alpha^2 + {}^3/_7\Delta g_{xy} + \Delta g_z) \tag{3}$$

$$A_{xy} = P(-K\alpha^2 + {}^2/_7\alpha^2 + {}^{11}/_{14}\Delta g_{xy}) \tag{4}$$

values are the *g*-shifts from the free electron value of 2.0023, and the free ion spin−orbit coupling constant λ of copper(II) (828 cm^{-1}) is reduced by the spin−orbit reduction parameters k_z and k_{xy}. The isotropic Fermi parameter *K* for copper(II) has been estimated as 0.43,[36] $P = g_e g_N \beta_e \beta_N \langle r^{-3} \rangle$ was estimated as 0.036 cm^{-1} for copper(II) complexes,[37] and α^2 represents the fractional unpaired spin density in the d$_{x^2-y^2}$ orbital. With the high-energy transition of the square planar complex [Cu-(**1**)(**2**)]$^{2+}$ (E_{xy} = 22 217 cm^{-1}) a low g_z and a large A_z value were expected. The experimentally observed g_z value is among the smallest reported so far for complexes of this type. The relatively strong ligand field in the case of [Cu(**2**)$_2$(ClO$_4$)]$^+$ also leads to comparably high-energy electronic transitions, and therefore a relatively small g_z and a large A_z are observed. The *g* and *A* values of the macrocyclic compounds, where the geometries and ligand fields are dependent on the macrocycle hole sizes, with the 14-membered ring (**4**) leading to a planar CuN$_4$ arrangement and a relatively strong ligand field,[24] are qualitatively as expected from eqs 1−4 (see Table 7).

4. AOM Calculations. The electronic transitions and the *g* values have been analyzed quantitatively with AOM calculations using CAMMAG.[2,26,27] The ligand field splitting in a complex is dependent on the metal ion and the ligand atoms and inversely proportional to approximately the fifth or sixth

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Table 8. Basic Parameters Used for the Calculation of the Electronic Properties of Copper(II) Amines[a]

param	value	param	value
k	0.7	K	0.43
ζ^b	$-580\ \mathrm{cm}^{-1}$	P	$0.036\ \mathrm{cm}^{-1}$
$e_{\sigma_{xy}}(\mathrm{RNH_2})^c$	$6400\ \mathrm{cm}^{-1}$	α^2	0.74
$e_{\sigma_{xy}}(\mathrm{R_2NH})^d$	$6700\ \mathrm{cm}^{-1}$		

[a] See text for the meaning of the parameters and the way in which the effects of ds mixing and the axial ligands are included. [b] Spin−orbit coupling ($\lambda^{\mathrm{Cu(II)}} = -828\ \mathrm{cm}^{-1}$). [c] Primary amine for Cu−N = 2.027 Å and $\alpha = 0°$. [d] Secondary amine for Cu−N = 2.027 Å and $\alpha = 0°$.

power of the metal−ligand distance *r*.[38−41] When bonding parameters for copper(II) amines, involving a separate parametrization for different degrees of alkyl substitution on amines[7] and corrections for bond length differences, assuming a $1/r^5$ or $1/r^6$ dependence, were used in the calculations, the estimated transition energies and *g* values did not agree satisfactorily with the observed parameters for all nine complexes.

From the structural data it emerges that the M−N vector does not always coincide with the calculated direction of the amine sp^3 orbital involved in the Cu−amine σ bond (angle α, see Table 6 and Chart 1). Although bent bonds have been analyzed in a number of transition metal complexes,[42] so far they have not been used in the analysis of copper(II) amines. Misdirected valences are expected to lead to a reduction of σ-bonding and a concomitant effective increase of π-bonding parameters. The reduction of the σ-bonding energy may be modeled by considering the projection of the direction of the amine sp^3 orbital to the Cu−L vector (cos α; see Chart 1), the effect being to reduce the interaction energy to $(\cos^2\alpha)\cdot e_\sigma$. Misdirection of the nitrogen lone pair will also change the energies of the $d_{xy,xz,yz}$ levels, leading to an additional lowering of the transition energies. At the present level of accuracy and with the relatively small deviations from linear bonds (see Table 6) a neglect of this latter effect does not seem to be unreasonable. Although CAMMAG allows a more general treatment of bent bonds (σ and π effects) via $e_{\pi\sigma}$ terms, we have chosen the above, admittedly less rigorous, approach since the complete treatment would have needed evaluation of a series of $e_{\pi\sigma}$ parameters and in our MM−AOM model we wanted to keep the transferable parameters to a minimum. The data presented in Table 7 indicate that with the parametrization given in Table 8, and with only correction for the reduced σ-bonding of in-plane ligands due to misdirected valences, generally reasonable overall agreement between experimental and computed spectroscopic data is found.

For planar and tetragonally distorted copper(II) complexes it is now well established that the energy of the d_{z^2} orbital is significantly affected by configuration interaction with the metal 4s orbital.[43] This effect may be accounted for by assigning each ligand an additional bonding parameter e_{ds}, and the computer program CAMMAG was modified to incorporate this change. For a planar complex, e_{ds} may be estimated directly from the energy of the $^2A_{1g}(z^2)$ excited state,[43] and for $[\mathrm{Cu}(\mathbf{1})(\mathbf{2})]^{2+}$ this yields the value $e_{\mathrm{ds}} \sim 1700\ \mathrm{cm}^{-1}$. This implies a ratio of e_{ds}: $e_\sigma \sim 1{:}4$ which is very similar to that derived from the electronic spectra of a range of planar complexes.[6] The value of e_{ds} was therefore set equal to $e_\sigma/4$ for each ligand in all the calculations. It was found that the bonding parameters derived for $[\mathrm{Cu}(\mathbf{1})(\mathbf{2})]^{2+}$, corrected for bond distance variation and for misdirected bonding, produced generally reasonable agreement with the observed spectral parameters. A slightly lower value of e_σ was assumed for the primary compared with the secondary amine groups, as had been deduced in earlier studies.[7] The basic values used for the e_σ parameters of the primary and secondary amines are listed in Table 8 for a Cu−N bond distance of 2.027 Å.

As the MM calculations used water as the axial ligand(s), bonding parameters appropriate to this ligand were used in MM−AOM calculations. These were taken from published plots of e_σ and e_π as a function of bond distance for the Cu−O interaction.[44] The same approach was used for the axial ligands in the AOM calculations based upon the structures revealed by X-ray analysis, where oxygen was the axial ligand atom, this being the case for every complex except $[\mathrm{Cu}(\mathbf{3})\mathrm{X}]^+$ and $[\mathrm{Cu}(\mathbf{5})\mathrm{X}_2]$. In both of these, axial ligation is by chloride, and here the parameters were estimated by correcting the values $e_\sigma = 5285$, $e_{\pi x} = e_{\pi y} = 885$, and $e_{\mathrm{ds}} = 1530\ \mathrm{cm}^{-1}$, reported for this ligand in planar $\mathrm{CuCl_4}^{2-}$, for the differences in bond length (Cu−Cl = 2.261 Å in planar $\mathrm{CuCl_4}^{2-}$).[45]

The calculated dd transitions and *g* values of the entire set of compounds, calculated using the basic parameters listed in Table 8, are compared with the experimental values in Table 7. Agreement is generally reasonable except for the $E_2(xz)$ transition of $[\mathrm{Cu}(\mathbf{3})\mathrm{X}]^+$ calculated by the MM−AOM procedure, which is $4500\ \mathrm{cm}^{-1}$ lower than the observed value. However, in this case the calculated and experimental data are not strictly comparable. This is because the MM structure involves water as the axial ligand, and the calculations suggest a rather short bond to this group, with this deviating substantially from the normal to the $\mathrm{CuN_4}$ plane. This leads to a low energy for the $E_2(xz)$ transition. However, experimental data are available only for a compound with chloride as the axial ligand, and the AOM calculations based on the crystal structure of this compound are in reasonable agreement with experiment.

The only other large deviations (>~10%) are for $[\mathrm{Cu}(\mathbf{1})(\mathbf{2})]^{2+}$, where the MM−AOM transitions are ~12% too low, and $[\mathrm{Cu}(\mathbf{3})(\mathrm{ClO_4})_2]$, where they are too high by about the same amount. In the former case, this is probably caused by the slight tetrahedral twist (8°), suggested by the MM calculation, which is not observed in practice (see preceding section). Here, the AOM transition energies estimated using the crystal structure agree reasonably well with the experiment. The high transition energies estimated for $[\mathrm{Cu}(\mathbf{3})(\mathrm{ClO_4})_2]$ in both the MM−AOM and AOM calculations are related to the short bond lengths suggested by the MM refinement of this complex, which are also indicated by the X-ray analysis. For copper(II) complexes, axial coordination is usually accompanied by a lengthening of the in-plane bonds, but the Cu−N bond distances in $[\mathrm{Cu}(\mathbf{3})(\mathrm{ClO_4})_2]$ are actually slightly shorter that those in the four-coordinate $[\mathrm{Cu}(\mathbf{1})(\mathbf{2})]^{2+}$ complex (see *Table 6*), being in fact very close to the "strain-free" value of 1.97 Å, used in the MM calculations.[5] We are currently attempting to redetermine the crystal structure of $[\mathrm{Cu}(\mathbf{3})(\mathrm{ClO_4})_2]$ to investigate this aspect further.

5. Calculation of EPR Hyperfine Parameters. For rhombically distorted systems with a $d_{x^2-y^2}$ ground state the coefficients C_1, C_2, and C_3 describe contributions from the lower energy d_{xy}, d_{xz}, and d_{yz} orbitals to the hyperfine constants. On the basis of a conventional molecular orbital description of metal−ligand bonding, these parameters are a function of the coefficients α, β, and γ of $d_{x^2-y^2}$, d_{xy}, and $d_{xz,yz}$ in the appropriate

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molecular orbital (eqs 5−7).[46,47] For systems with rhombic

$$C_1 = \frac{-\alpha^2\beta^2\lambda}{E_{xy}} \quad (5)$$

$$C_2 = \frac{-\alpha^2\gamma^2\lambda}{E_{yz}} \quad (6)$$

$$C_3 = \frac{-\alpha^2\gamma^2\lambda}{E_{xz}} \quad (7)$$

geometries a modification of the equations for the calculation of g and A values (eqs 1−4) has been proposed,[47] and substitution of the coefficients C_1, C_2, and C_3 for $\Delta g_{x,y,z}$ leads to eqs 8−10. Here α^2 represents the fractional time that the

$$A_x = P\Bigg[-K\alpha^2 + {}^2/_7\alpha^2(a^2 - b^2) + {}^4/_7(3^{1/2})\alpha^2ab + 2C_2 - \frac{(3a - 3^{1/2}b)2C_3}{14(a + 3^{1/2}b)} - {}^8/_7C_1\frac{b}{a}\Bigg] \quad (8)$$

$$A_y = P\Bigg[-K\alpha^2 + {}^2/_7\alpha^2(a^2 - b^2) - {}^4/_7(3^{1/2})\alpha^2ab + 2C_3 - \frac{(3\mathrm{a} - 3^{1/2}b)2C_2}{14(\mathrm{a} - 3^{1/2}b)} + {}^8/_7C_1\frac{b}{7}a\Bigg] \quad (9)$$

$$A_z = P\Bigg[-K\alpha^2 + {}^2/_7\alpha^2(a^2 - b^2) + \frac{(3a - 3^{1/2}b)2C_3}{14(a + 3^{1/2}b)} + \frac{(3a + 3^{1/2}b)2C_2}{14(a - 3^{1/2}b)} + 8C_1\Bigg] \quad (10)$$

unpaired electron spends in the metal d orbital and the coefficients a and b represent the relative contributions of $d_{x^2-y^2}$ and d_{z^2} to the metal part of the ground state wave function ($\psi = a\ (d_{x^2-y^2}) - b\ (d_{z^2})$; $a^2 + b^2 = 1$). The mixing coefficient b may be estimated from eqs 11−13, appropriate to a rhombic g

$$\Delta g_x = \frac{-2\lambda k_x^{\,2}(\mathrm{a} - \sqrt{3}b)^2}{E_{yz}} \quad (11)$$

$$\Delta g_y = \frac{-2\lambda k_y^{\,2}(a - \sqrt{3}b)^2}{E_{xz}} \quad (12)$$

$$\Delta g_z = \frac{-8\lambda k_z^{\,2}a^2}{E_{xy}} \quad (13)$$

tensor. On the basis of eqs 3 and 4 and using experimentally available g shifts, $\alpha^2 = 0.74$ is estimated. This value is as expected on the basis of results with similar copper(II) complexes.[46] Substitution of the value of b estimated from the calculated g values of all 10 complexes, together with C_1, C_2, and C_3, yields the estimated hyperfine values listed in Table 7. Agreement between the parameters estimated using the structures derived from MM calculations and those derived using the observed structures is reasonable.

Conclusion

The MM−AOM method allows the prediction of electronic transitions and spin Hamiltonian parameters of copper(II) tetraamines without prior knowledge of structural or electronic properties of the compounds. These predictions are based on a constant parametrization of the MM and the AOM model, and the calculated spectroscopic properties are in reasonable agreement with the observed data. The range of compounds tested so far include four-, five-, and six-coordinate complexes with Cu−N bonds (in-plane) of 1.98−2.08 Å, Cu−X bonds (axial ligands) of 2.4−2.8 Å, bond distortion angles α (see Chart 1) from 0 to 16°, and tetrahedral distortion angles ∅ (see Chart 1) from 0 to 36° and results in electronic transitions (d_{xy} transition) from 17 200 to 22 200 cm^{-1}, g_z values from 2.21 to 2.14, and A_z values from 184 × 10^{-4} to 200 × 10^{-4} cm^{-1}, with averaged error limits (calculated (MM−AOM) vs experimental parameter) of ∼< 5% for electronic transitions and A values and ∼< 1% for g values. The calculated electronic parameters based on experimental and computed (MM) structural data with the same, constant set of electronic parameters are of similar quality; viz., the inaccuracy of strain energy minimized structures is not the limiting factor in the estimation of electronic properties.

The main assumptions adopted are (i) that a constant set of e-parameters, only dependent on the type of amine, the Cu−N bond distance, and direction of the amine σ-orbital are used, (ii) that π-interactions due to misdirected valences in the xy-plane have been neglected, (iii) that a constant ratio of $e_{\sigma z}$ vs e_{ds} (4s − 3d_{z^2} configuration interaction) has been adopted, and (iv) that the orbital coefficients α, β, and γ have been kept constant. While these simplifications may not be rigorously justifiable, they are a necessity for a model that is useful for the design of new compounds with given spectroscopic properties and/or for the characterisation of solution structures. The empirical set of parameters, deduced in a thorough spectroscopic analysis, partly based on single-crystal data, limits its application to the rather broad class of copper(II) tetraamines with a wide variety of structures where it leads to satisfactory results. The applicability of the MM−AOM method to other copper(II) systems is being evaluated. A worthwhile extension is to include other relevant ligand systems such as imines, carboxylates, thioethers, thiols, ethers, and alcohols, as force field parameters for these systems have been described[5] or evaluated.

Supporting Information Available: Tables of complete crystal data, anisotropic thermal parameters, hydrogen atom coordinates, and U values, bond lengths, bond angles, and torsional angles (Tables S1−S8) (9 pages). Ordering information is given on any current masthead page.

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