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Synthesis and Characterization of Copper(II)–Acetazolamide (5-Acetamido-1,3,4-thiadiazole-2-sulfonamide) Complexes. Crystal Structure of Dimeric $[\text{Cu}(\text{Acm})(\text{NH}_3)_2(\text{OH}_2)]_2 \cdot 2\text{H}_2\text{O}$

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The synthesis and characterization of four copper(II) complexes with the deprotonated acetazolamide ligand (Acm) are described. The crystal and molecular structures and IR spectra of $[\text{Cu}(\text{Acm})(\text{NH}_3)_2(\text{OH}_2)]_2 \cdot 2\text{H}_2\text{O}$ (I) are reported and compared with the crystal and molecular structures and IR spectra of $\text{Ni}(\text{Acm})_2(\text{NH}_3)_4$, described in a previous paper. The copper(II) compound crystallizes in the triclinic space group $P\bar{1}$, $Z = 1$, with the cell dimensions $a = 7.548$ (4) Å, $b = 8.205$ (17) Å, $c = 10.797$ (3) Å, $\alpha = 93.59$ (6)°, $\beta = 108.68$ (3)°, and $\gamma = 98.50$ (9)°. The structure was solved by direct methods and refined by least-squares calculations to a conventional R factor of 7.0% for 1867 counter data. The structure consists of discrete dimeric $[\text{Cu}(\text{Acm})(\text{NH}_3)_2(\text{OH}_2)]_2$ units and uncoordinated water molecules. The metal ions in the dinuclear entity are linked through two N–N groups from the thiadiazole rings, which belong to two adjacent Acm ligands, forming with the bridging atoms a six-membered ring. Each copper(II) ion shows a tetragonally elongated octahedral geometry. The electronic, IR, and EPR data are consistent with the crystal structure. The study of reciprocal molar susceptibility vs temperature indicates that there is no appreciable interaction between copper ions. Magnetic and EPR data of the other compounds synthesized suggest a different environment for the copper(II) ions.

Introduction

Interest in the coordination behavior of acetazolamide (5-acetamido-1,3,4-thiadiazole-2-sulfonamide; Acm) arises from several reasons. Acm is a diuretic sulfonamide used clinically, whose therapeutic action can be explained from the potent inhibition of the Zn(II) metalloenzyme carbonic anhydrase. There is much evidence reported in the literature, including crystal structures and spectral data, that shows the inhibitor reacting with the enzyme by direct coordination with the metal.^{1,2} Although the sulfonamido deprotonated moiety is generally considered the portion of the Acm that interacts with the Zn(II), there is no solid experimental basis to state this.³ So, it seemed interesting to investigate which are the best coordination positions of the Acm molecule, which has two ionizable protons and several donor atoms. On the other hand, since this ligand presents a diazole group, the complexes of Acm and essential trace ions could represent one of the simplest models for the natural metalloenzymes. In fact, X-ray data have shown that the Zn(II) ion in carbonic anhydrase is bound to three histidyl imidazole nitrogens.⁴

In a previous paper,^{5a} we have reported the synthesis and characterization of Zn(II) and Co(II) complexes of Acm. Spectroscopic data suggest that coordination to the metal is produced through the sulfonamido deprotonated group, which is consistent with the models proposed by Kannan and Dunitz. However, a more recent work^{5b} in which the crystal structure of a Ni(II) complex of Acm is described, shows the ligand deprotonated in the acetamido group, the donor atom being N(2) of the thiadiazole ring. This behavior is completely different from that the previously observed.

In the present paper we have synthesized four copper complexes of Acm. The crystal structure of one of them, $[\text{Cu}(\text{Acm})(\text{NH}_3)_2(\text{OH}_2)]_2 \cdot 2\text{H}_2\text{O}$ (I), presents the ligand deprotonated both in the acetamido and in the sulfonamido positions, which allows us to better understand the two preceding different coordination behaviors of Acm. Furthermore, a comparison between the crystalline structure of both complexes, $\text{Ni}(\text{Acm})_2(\text{NH}_3)_4$ and $[\text{Cu}(\text{Acm})(\text{NH}_3)_2(\text{OH}_2)]_2 \cdot 2\text{H}_2\text{O}$, leads us to conclusions about the best ligand donor atom. Finally, the combined study of crystallographic results and IR spectra supplies a useful tool to determine the mode of binding of the title ligand when no single crystals of the compounds are available.

As for the other three complexes of copper–Acm reported here, the magnetic and EPR data indicate that although $\text{Cu}(\text{Acm})$

$(\text{NH}_3)_3$ (II) and $\text{Cu}(\text{Acm})(\text{NH}_3) \cdot \text{H}_2\text{O}$ (III) present the same Cu:Acm molar ratio as the title crystalline copper complex, the metal environment must be different.

Experimental Section

Acm was supplied as a powder material by Cyanamid Laboratories. All reagents used were of analytical grade.

Synthesis of $\text{Cu}(\text{Acm})(\text{NH}_3)_3$ (II). Solid Acm (3 mmol) was dissolved in a hot solution of CuCl_2 (1 mmol in 100 cm³ of ethanol) (molar ratio Acm:Cu(II) = 3:1) by heating and stirring. Then, heating was stopped and 1 cm³ of concentrated ammonia (ca. 11 M) was added slowly drop by drop. When the mixture was stirred for ca. 5 min, a blue microcrystalline precipitate started to separate. The solid that deposited was collected by filtration, washed with ethanol, and dried in vacuo. Yield: ca. 90% based on metal. Anal. Calcd for $\text{C}_4\text{H}_{13}\text{CuN}_7\text{O}_3\text{S}_2$ ($M_r = 334.8$): C, 14.3; H, 3.9; N, 29.3; Cu, 19.0. Found: C, 14.2; H, 3.8; N, 29.2; Cu, 18.7.

Synthesis of $[\text{Cu}(\text{Acm})(\text{NH}_3)_2(\text{OH}_2)]_2 \cdot 2\text{H}_2\text{O}$ (I). Solid Acm (3 mmol) was dissolved in a hot solution of CuCl_2 (1 mmol in 100 cm³ of ethanol) (molar ratio Acm:Cu(II) = 3:1) by heating and stirring. Then, heating was stopped and 2 cm³ of concentrated ammonia was added quickly in order to avoid the precipitation of the former compound. If turbidity appeared, ammonia was added until redissolution of the precipitate was achieved. In any case the reaction mixture was reduced in volume to 30 cm³ by heating and allowed to stand at room temperature. After several hours a precipitate was observed. Then, half of the volume of the liquid was separated by decantation, being substituted by the same volume of ethanol (so, the solution was diluted). The precipitate was redissolved again by adding the necessary volume of concentrated ammonia (ca. 20 cm³). This last solution was reduced in volume to 30–40 cm³ by heating and allowed to stand at 4–5 °C. Single crystals of the compound started to appear after 5–15 days of cooling. Crystals were separated by filtration with a Millipore filter, washed with ethanol, and dried in vacuo. The crystals degrade slowly at room temperature, probably due to the loss of NH_3 . Anal. Calcd for $\text{C}_8\text{H}_{28}\text{Cu}_2\text{N}_{12}\text{O}_{10}\text{S}_4$ ($M_r = 707.7$): C, 13.6; H, 3.9; N, 23.7; Cu, 17.9. Found: C, 13.6; H, 3.5; N, 24.3; Cu, 18.3. One of these crystals was selected for X-ray crystallographic analysis.

Synthesis of $\text{Cu}(\text{Acm})(\text{NH}_3) \cdot \text{H}_2\text{O}$ (III). To a methanolic solution of Acm (10 mmol in 500 cm³) were added first 5 cm³ of concentrated ammonia and then, after the solution was stirred for several minutes, a

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Table I. Crystallographic Data for $[\text{Cu}(\text{Acm})(\text{NH}_3)_2(\text{OH}_2)]_2 \cdot 2\text{H}_2\text{O}$

chem formula	$\text{C}_8\text{H}_{28}\text{Cu}_2\text{N}_{12}\text{O}_{10}\text{S}_4$
fw	707.7
space group	$P\bar{1}$ (No. 2)
cell	$a = 7.458$ (4) Å, $b = 8.205$ (17) Å, $c = 10.797$ (3) Å, $\alpha = 93.59$ (6)°, $\beta = 108.68$ (3)°, $\gamma = 98.50$ (9)°
V	614 (1) Å ³
Z	1
$\rho_{\text{obsd}}, \rho_{\text{calcd}}$	1.90, 1.91 g cm ⁻³
$\mu_{\text{Mo K}\alpha}$	20.90 cm ⁻¹
transm coeff	0.85–0.78
T	20 °C
$\lambda_{\text{Mo K}\alpha}$	0.709 26 Å
R^a	0.070
R_w^a	0.090

$$^a R = (\sum ||F_o| - |F_c||) / (\sum |F_o|); R_w = [\sum w|F_o| - |F_c|]^2 / \sum w|F_o|^2]^{1/2}.$$

methanolic solution of CuCl_2 (3 mmol in 125 cm³) (molar ratio Acm:Cu(II) = 3:1). Finally, 25 cm³ of concentrated ammonia was added drop by drop. After the mixture was stirred for 4–5 min, a blue precipitate started to separate. The suspension was allowed to stand for 15 min. Then, the blue microcrystalline solid was collected by filtration and washed with methanol. The product obtained by this method was heated in a stove at 80 °C for 3 days, giving an amorphous blue greenish solid, which was analyzed. Yield: ca. 75% based on metal. Anal. Calcd for $\text{C}_4\text{H}_8\text{CuN}_2\text{O}_4\text{S}_2$ ($M_r = 318.8$): C, 15.1; H, 2.8; N, 22.0; Cu, 19.9. Found: C, 15.0; H, 2.7; N, 22.0; Cu, 19.9.

Synthesis of $\text{Cu}_2(\text{Acm})(\text{OH})_4 \cdot 3\text{H}_2\text{O}$ (IV). The complex was obtained by mixing methanolic solutions containing Acm (3 mmol in 150 cm³) and CuCl_2 (13.5 mmol in 500 cm³) (molar ratio Acm:Cu(II) = 1:4.5). Then, concentrated ammonia was added by dropping with continuous stirring. After addition of 60 drops (ca. 3 cm³ in total), a green voluminous precipitate started to separate. The suspension was allowed to stand for 2 days, and the solid was collected by filtration, washed several times with methanol, and dried in vacuo. Yield: ca. 65% based on Acm. Anal. Calcd for $\text{C}_4\text{H}_{14}\text{Cu}_3\text{N}_4\text{O}_{10}\text{S}_2$ ($M_r = 532.9$): C, 9.0; H, 2.6; N, 10.5; Cu, 35.8. Found: C, 9.1; H, 2.0; N, 10.7; Cu, 35.4.

Analyses were carried out for C, H, and N by elemental analysis and for copper by atomic absorption spectroscopy. Percentages of $\text{H}_2\text{O}/\text{OH}^-$ and NH_3 were confirmed by thermogravimetric studies.

The X-ray powder patterns of the four compounds have been recorded, showing that the complexes I and II are crystalline but not isomorphous. The compounds III and IV are amorphous.

Physical Measurements. Infrared spectra of KBr/CsI pellets were recorded on a Perkin-Elmer 843 instrument. Electronic spectra in the UV–vis range were obtained with a Perkin-Elmer Lambda 15 spectrophotometer. Electronic spectra in the near-IR region were registered with a Perkin-Elmer Lambda 9 spectrophotometer. EPR spectra of polycrystalline samples and frozen solutions were recorded at X-band frequencies with a Bruker ER 200D spectrometer equipped with a liquid-N₂ continuous-flow cryostat.

Magnetic susceptibility data were collected on powdered samples of the compounds with use of a Faraday-type magnetometer fitted with a helium continuous-flow cryostat. Mercury tetrakis(thiocyanato)cobaltate was used as a susceptibility standard. All data were corrected for diamagnetism with the appropriate Pascal constants.

The X-ray powder diffraction patterns were obtained through a Kristalloflex 810 Siemens diffractometer using $\text{Cu K}\alpha$ radiation.

Crystallographic Data Collection and Refinement of the Structure. Crystallographic data are summarized in Table I. The crystal used was blue with a prismatic shape. The X-ray data were recorded with a CAD-4 Enraf-Nonius diffractometer using the graphite-monochromated $\text{Mo K}\alpha$ radiation. Cell dimensions were obtained by a least-squares fit from the setting angles of 25 well-centered reflections with $6^\circ \leq 2\theta \leq 26^\circ$. A total of 2300 reflections ($\pm h, \pm k, l$; $2 < 2\theta < 50^\circ$) were measured with the variable-speed ω - 2θ scan technique, of which 2144 were unique, and 1867 with $I > 2.5\sigma(I)$ were used in the refinement. Lorentz and polarization corrections were applied but not for absorption. The space group $P\bar{1}$ was assumed throughout the structure analysis and was confirmed by the successful refinement of the structure. The positions of copper and eight non-hydrogen atoms were determined by direct methods (MULTAN 11/84).⁶ The remaining non-hydrogen atoms were located from

Table II. Bond Distances and Angles

Distances (Å)			
O(4)–Cu	2.011 (4)	N(4)–S(2)	1.576 (4)
N(1)–Cu	2.546 (4)	C(1)–S(2)	1.744 (5)
N(4)–Cu	2.028 (4)	C(3)–O(1)	1.246 (6)
N(5)–Cu	2.012 (4)	N(2)–N(1)	1.374 (6)
N(6)–Cu	2.825 (6)	C(1)–N(1)	1.294 (6)
N(2)*–Cu	2.020 (4)	C(2)–N(2)	1.339 (6)
C(1)–S(1)	1.729 (5)	C(2)–N(3)	1.341 (6)
C(2)–S(1)	1.748 (5)	C(3)–N(3)	1.342 (7)
O(2)–S(2)	1.433 (4)	C(4)–C(3)	1.506 (7)
O(3)–S(2)	1.443 (4)		
Angles (deg)			
N(1)–Cu–O(4)	96.0 (2)	C(1)–S(2)–O(3)	103.6 (2)
N(4)–Cu–O(4)	91.5 (2)	C(1)–S(2)–N(4)	104.8 (2)
N(4)–Cu–N(1)	78.7 (2)	N(2)–N(1)–Cu	139.5 (3)
N(5)–Cu–O(4)	168.0 (2)	C(1)–N(1)–Cu	107.6 (3)
N(5)–Cu–N(1)	95.6 (2)	N(1)*–N(2)*–Cu	120.5 (3)
N(5)–Cu–N(4)	93.6 (2)	C(2)*–N(2)*–Cu	125.9 (3)
N(6)–Cu–O(4)	80.6 (2)	C(1)–N(1)–N(2)	112.2 (4)
N(6)–Cu–N(1)	162.4 (1)	C(2)–N(2)–N(1)	113.3 (4)
N(6)–Cu–N(4)	84.1 (2)	C(3)–N(3)–C(2)	119.3 (4)
N(6)–Cu–N(5)	89.2 (2)	S(2)–N(4)–Cu	117.9 (2)
N(2)*–Cu–O(4)	85.9 (2)	S(2)–C(1)–S(1)	125.0 (3)
N(2)*–Cu–N(1)	98.7 (2)	N(1)–C(1)–S(1)	115.3 (3)
N(2)*–Cu–N(4)	176.1 (2)	N(1)–C(1)–S(2)	119.6 (4)
N(2)*–Cu–N(5)	89.6 (2)	N(2)–C(2)–S(1)	112.1 (3)
N(2)*–Cu–N(6)	98.3 (2)	N(3)–C(2)–S(1)	127.1 (4)
C(2)–S(1)–C(1)	87.0 (2)	N(3)–C(2)–N(2)	120.7 (4)
O(3)–S(2)–O(2)	118.2 (2)	N(3)–C(3)–O(1)	124.3 (4)
N(4)–S(2)–O(2)	114.1 (2)	C(4)–C(3)–O(1)	120.0 (5)
N(4)–S(2)–O(3)	109.4 (2)	C(4)–C(3)–N(3)	115.8 (5)
C(1)–S(2)–O(2)	105.1 (2)		

successive Fourier synthesis. Refinement of the structure was carried out with the SHELX 76 system⁷ by weighted anisotropic full-matrix least squares. Positions of 13 hydrogen atoms (of the 14 in the asymmetric unit) were determined by Fourier difference synthesis and included as fixed parameters in the final refinement with common fixed isotropic thermal parameters ($U = 0.077$ Å²). At this stage of the refinement, due to the difficulty in inferring the site occupied by the coordination water molecule in the copper polyhedron, three different attempts of refinement were made by taking into account the available positions. Evaluation of the resulting R factors and thermal parameters for the involved nitrogen and oxygen atoms in these models indicates small differences favorable to the proposed structure. Moreover, in the difference map the positions of the six hydrogen atoms corresponding to the two ammonia molecules were clearly located.

In the final difference map the residual maximum was a peak of 1.6 e Å⁻³ located near the copper atom. Atomic scattering factors and corrections for anomalous dispersion for the Cu atom were taken from ref 8. The geometrical calculations were performed with XANADU⁹ and DISTAN,¹⁰ and molecular illustrations were drawn with the ORTEP plotting program.¹¹ Bond lengths and bond angles are tabulated in Table II. Full information concerning conditions for crystallographic data collection and structure refinement, positional parameters, hydrogen atom coordinates, anisotropic thermal parameters, equations of least-squares planes, hydrogen bond distances, and observed and calculated structure factors are given in the supplementary material (Tables S1–S7).

Results and Discussion

Description of the Structure. Coordination Polyhedron. Figure 1 shows an ORTEP drawing of complex I with the atomic numbering and thermal ellipsoids.

The structure consists of discrete dimeric $[\text{Cu}(\text{Acm})(\text{NH}_3)_2(\text{OH}_2)]_2$ centrosymmetric units and uncoordinated water molecules that provide crystalline stability through a network of hydrogen

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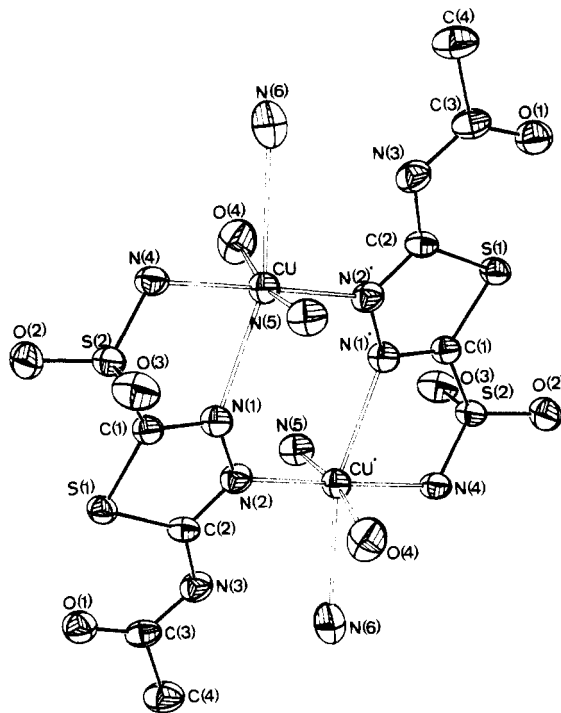


Figure 1. ORTEP drawing of $[\text{Cu}(\text{Acm})(\text{NH}_3)_2(\text{OH}_2)]_2 \cdot 2\text{H}_2\text{O}$ (I), showing the atomic numbering and thermal ellipsoids.

bond interactions. The copper ions in the dinuclear entity are linked through two N–N groups from the thiazadiazole rings which belong to two adjacent Acm ligands, forming with the bridging atoms a six-membered ring. Each copper ion shows a tetragonally elongated octahedral geometry, the four basal ligands being one sulfonamide nitrogen atom [N(4)] from one Acm molecule, one thiazadiazole nitrogen atom [N(2)*] from an adjacent Acm ligand, one ammonia nitrogen atom [N(5)], and one water oxygen atom [O(4)]. The axial sites are occupied by the second thiazadiazole nitrogen atom from the first Acm molecule [N(1)] and one ammonia nitrogen atom [N(6)]. The four equatorial bond lengths are similar in spite of the donor atoms belonging to four different groups. The basal coordination plane is tetrahedrally distorted, with atomic deviations from the best fit plane, defined by the donor atoms N(2)*, N(4), N(5), and O(4), ranging from -0.12 to $+0.12$ Å; the copper ion lies 0.07 Å above this plane, being displaced toward the apical position occupied by the atom N(1).

The axial donor atoms are placed at distances longer than the basal ones [Cu–N(1) = 2.546 (4) and Cu–N(6) = 2.825 (6) Å] and significantly different, thus leading to a coordination $4 + 1 + 1$ for the copper ion. The very long Cu–N(6) bond length suggests a weak interaction with the metal, described by other authors as a semicoordination. However, the interatomic angles N(6)–Cu–L [L = N(1), N(2)*, N(4), N(5), O(4)] fall within the range of an octahedral environment.

If we compare the dimensions of the coordination polyhedron of the present complex with those of the compound $\text{Ni}(\text{Acm})_2(\text{NH}_3)_4$, previously reported,^{5b} we can observe that, in the equatorial plane, the Cu–NH₃ bond length is shorter than the Ni–NH₃ one. It is also interesting to note that while in the copper complex the axial distances are considerably longer than the basal ones, in the nickel compound the six distances present values of the same order (from 2.15 to 2.09 Å). The distortion in the copper complex, mainly as far as the axial distances and the coordination angles are concerned, is due to the donor atom sites in the ligand, which force the geometry around the metal.

Ligand Conformation. A comparison of the previously reported structure of Acm in the Ni(II) complex^{5a} with the structure of the ligand in the title Cu(II) compound shows several interesting aspects correlated well with a different deprotonation (and thus a different coordination behavior) of the Acm in both complexes: whereas in the Ni(II) complex Acm is monodeprotonated (deprotonation takes place through the acetamido group), in the

Cu(II) complex it is doubly ionized by loss of the acetamido and sulfonamido protons.

So, with regard to the internal geometry of Acm, in the Ni(II) complex the ligand bond lengths modified are just those corresponding to the acetamido moiety, as well as C(2)–N(2), C(2)–S(1), and S(2)–N(4). As for the Cu(II) complex, all bond lengths change with the exception of N(1)–N(2), C(1)–S(2), and S(2)–O(3).

The distance N(1)–N(2) in the title compound [1.374 (6) Å] is comparable to that found in the ligand¹² [1.372 (3) Å] and in the Ni(II) complex [1.376 (6) Å], indicating that the bonds of N(2) and N(1) with the metal ions have no influence in this length. The N(2)–C(2) bond length is longer in the present complex [1.339 (6) Å] than in Acm [1.311 (3) Å] and even than in the Ni(II) complex [1.330 (7) Å], whereas the N(1)–C(1) distances are similar in the three compounds [1.294 (6) Å for the Cu(II) complex; 1.302 (8) Å for the Ni(II) complex; 1.294 (3) Å for Acm]. The reduction of the N(2)–C(2) bond order is consistent with the decrease of electronic density owing to the coordination and with the important increase of the C(2)–N(3) order bond. On the contrary, the N(1)–C(1) distance does not change probably because the interaction N(1)–Cu(II) is weaker than N(2)–Cu(II) and because the C(1)–S(2) bond length remains unaltered.

The Ni(II) and Cu(II) complex crystal structures seem to indicate that the thiazadiazole ring N(2) atom must be the best donor atom of the acetazolamide, since it is the ligand atom selected by Ni(II) and presents the shortest ligand atom–metal distance in the copper complex. The reason that N(2) is a better donor atom than N(1) could be the fact that there is a stronger interaction between the ring and the acetamido group than between the ring and the sulfonamido one. As the acetamido group and the thiazadiazole ring are conjugated, the negative charge over the acetamido group nitrogen atom is able to move through N(3)–C(2)–N(2) and, consequently, the decrease of negative charge on N(2) is stabilized. On the other hand, the C(1)–S(2) distance is one of the few ligand distances that remains constant in both complexes, corroborating the independence between the sulfonamido group and thiazadiazole ring.

The changes in the acetamido group are similar to those found in the Ni(II) complex, as can be expected, because they are due mainly to the deprotonation. The C(2)–N(3) and N(3)–C(3) bond lengths are shorter in the complexes than in the ligand [1.341 (6) and 1.342 (7) Å for the Cu(II) complex and 1.369 (3) and 1.355 (3) Å for the ligand, respectively], consistent with partial double-bond character, while C(3)–O(1) is longer [(1.246 (6) Å for the Cu(II) complex; 1.222 (2) Å for the ligand)], which is consistent with a hydrogen bonded to the oxygen and/or with a concentration of the electronic density on the O(1) atom by way of resonance forms.

The sulfonamido group presents the most significant differences between the Cu(II) and the Ni(II) complexes. In the Ni(II) compound the S(2)–O(2) and S(2)–O(3) distances are similar to the equivalent ones of Acm, whereas in the Cu(II) complex the S(2)–O(2) one is slightly longer and the S(2)–O(3) distance considerably longer [1.433 (4) and 1.443 (4) Å for the Cu(II) complex and 1.426 (2) and 1.425 (2) Å for the ligand, respectively]. Furthermore, the S(2)–N(4) bond length of the first complex is a bit longer than the corresponding distance of Acm, while the same distance in the Cu(II) one has suffered as an important decrease [1.594 (3) Å for Acm; 1.576 (4) Å for the Cu(II) complex]. The modifications observed in this group in the title copper(II) complex come from the deprotonation and the following delocalization of the negative charge through the N(4)–S(2)–O(3) bonds.

In conclusion, it should be noticed that (a) in spite of deprotonation, acetamidato anion does not interact with the metal and the sulfonamidato anion acts only as a unidentate ligand and (b) it is clear from the crystal structures of the Ni(II) and Cu(II) complexes that acetazolamide can bind in two different coordination modes depending upon the nature of the metal ion.

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Table III. Important Infrared Spectral Bands of Acm and Acm Complexes^a (cm⁻¹)

compd	$\nu(\text{C}=\text{O})$	$\nu(\text{SO}_2)_{\text{asym}}$	$\nu(\text{SO}_2)_{\text{sym}}$
Acm	1672 s	1318 s	1170 s
Zn(Acm) ₂ (NH ₃) ₂	1699 s	1285 s	1145 s
Co(Acm) ₂ (NH ₃) ₂	1705 s	1290 s	1145 s
Ni(Acm) ₂ (NH ₃) ₄	1681 w, 1624 m	1328 s	1178 s
[Cu(Acm)(NH ₃) ₂ (OH ₂) ₂] ₂ ·2H ₂ O	1617 m	1296 s	1145–1126 s (doublet)
Cu(Acm)(NH ₃) ₃	1611 w	1289 m, 1245 m	1132 s
Cu(Acm)(NH ₃)·H ₂ O	1695 w, 1600 sh	1304 m-s	1146 vs
Cu ₃ (Acm)(OH) ₄ ·3H ₂ O	1615 sh	1303 m-s	1144 vs

^a Abbreviations: w = weak; m = medium; s = strong; vs = very strong; sh = shoulder.

Table IV. Electronic Spectral and Magnetic Data for the Compounds

compd	d-d ^a	MLCT ^a	intraligand ^a	g_{\parallel}	g_{\perp}	μ_{eff}^b
acetazolamide			34 364			
[CuAcm(NH ₃) ₂ (OH ₂) ₂] ₂ ·2H ₂ O (I)	16 700 14 800 ^c	27 000 s	31 646	2.25 2.40 ^c	2.06 2.11 ^c	1.84
CuAcm(NH ₃) ₃ (II)	16 260		30 581	2.06	2.13	1.73
CuAcm(NH ₃)·H ₂ O (III)	15 450	24 390 ^d	30 303 b	2.22	2.11	1.32
Cu ₃ Acm(OH) ₄ ·3H ₂ O (IV)	14 800		24 390 b	2.03	2.18	1.34

^a cm⁻¹. ^b μ_{B} at 298 K; s = shoulder; b = broad. ^c In DMF solution; all the other data correspond to solid samples. ^d Obtained by deconvolution of the experimental curve.

Crystal Packing. As in the nickel complex, the 1,3,4-thiadiazole ring of the copper complex is nearly planar (root mean square deviation 0.003 Å). However, the acetamido and sulfonamido groups are significantly more deviated from this plane in the present compound, as can be seen from the respective values of the angles between the mean planes S(1)N(1)N(2)C(1)C(2) and O(1)N(3)C(3)C(4) [3.3° in the Ni(II) complex; 9.6° in the Cu(II) compound] and the S(2) deviations from the ring plane (0.07 Å in the Ni complex; 0.15 Å in the title compound).

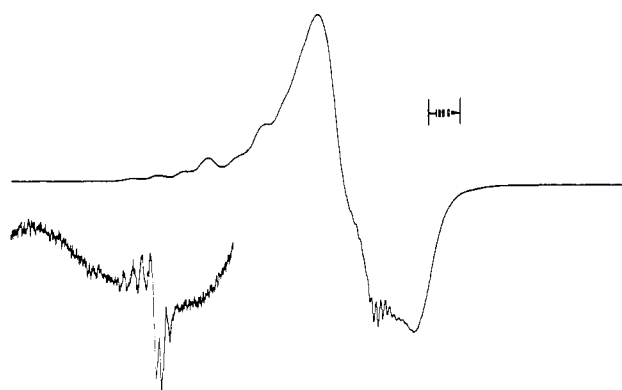
Within each dinuclear entity, the two copper atoms [separated 4.363 (1) Å] are related through crystallographic centers on the *ab* faces, forming the above-mentioned nearly planar six-membered ring with the bridging groups [i.e. Cu, N(1), N(2), Cu*, N(1)*, and N(2)*]. The angle formed between these rings and the *ab* plane is 45°. Interaction between dinuclear entities is made through a tridimensional network of hydrogen bonds involving ammonia molecules, the deprotonated nitrogen atom from the sulfonamide moiety, and water molecules.

Spectral and Magnetic Properties. IR Spectra. The more significant IR bands are given in Table III (it includes also the IR bands of the Zn(II), Co(II), and Ni(II) compounds previously reported).⁵ A comparison among the infrared spectra of the present Cu(II) complexes and those corresponding to the free ligand indicates that carbonyl and sulfonyl stretching bands have changed, as expected by deprotonation of both groups. It is interesting to note that while in the Zn(II) and Co(II) complexes the IR spectra exhibit the characteristic single strong band of the carbonyl group, in the Cu(II) compounds, as observed in the Ni(II) one, this band suffers a reduction in intensity to give weak bands and a shift to lower frequencies, indicating a reduction of the C=O bond order here even more pronounced than that in the Ni(II) complex.

As for the $\nu(\text{SO}_2)_{\text{sym}}$ and $\nu(\text{SO}_2)_{\text{asym}}$ vibrations, whereas in the Ni(II) compound these bands remain unchanged, in the four Cu(II) complexes, as it happens with the Zn(II) and Co(II) compounds, they are shifted to lower frequencies, especially the $\nu(\text{SO}_2)_{\text{sym}}$ one, suffering also a splitting in some cases.

It has not been possible to assign $\nu(\text{M}-\text{N})$ bands in the IR spectra of the four copper complexes because Acm presents many bands in this region.

All in all, these results suggest that the IR spectra of Acm derivatives may be used as diagnostic tools for the determination of the ligand coordination mode. Since the infrared bands indicate if acetamido and/or sulfonamido groups have or have not changed, from analogy with the two compounds whose crystalline structure is known, we will be able to propose how Acm coordinates to the metal: like in the nickel(II),^{5b} like in the copper(II) (I), or like in the Zn(II)/Co(II)^{5a} complexes.

**Figure 2.** EPR spectrum of a saturated DMF solution of I at 110 K.

EPR Spectra. EPR spectral parameters of the four complexes determined from powdered samples are listed in Table IV. EPR spectra of [Cu(Acm)(NH₃)₂(OH₂)₂]₂·2H₂O (I) and Cu(Acm)(NH₃)·H₂O (III) are typical of tetragonal copper(II) complexes with a $d_{x^2-y^2}$ ground state. The EPR spectrum of Cu(Acm)(NH₃)₃ (II) shows that $g_{\perp} > g_{\parallel}$, suggesting that the unpaired electron occupies the d_{z^2} orbital in a compressed tetragonally octahedral geometry (the lack of the d-d band at 11 000–12 000 cm⁻¹ in the vis spectra leads us to reject the possibility of a bipyramidal-trigonal geometry). Nevertheless, it is worth mentioning that although $g_{\perp} > g_{\parallel}$, if $g_{\parallel} > 2.00$ (as it happens in the present case), the compression could be just apparent.^{13,14} Finally, Cu₃(Acm)(OH)₄·3H₂O (IV) presents a broad undefined isotropic spectrum.

EPR spectra of compounds I and II exhibit a low-field absorption in the g_{\parallel} region barely visible as a shoulder, which is indicative of a $\Delta M_s = \pm 2$ forbidden transition in the triplet state and which in turn is consistent with the dimeric nature of the compound I.

EPR spectra of DMSO and DMF solutions of compounds I–III have been obtained (compound IV is insoluble in all the common apolar and polar solvents), with the EPR spectrum of a DMF saturated solution of compound I at 110 K being remarkable (see Figure 2). In the $\Delta M_s = \pm 1$ region, seven copper hyperfine lines, with an average spacing of 89 G, are seen on the g_{\parallel} component. The appearance of these lines is consistent with the existence of two copper ions in the molecule. The eighth signal must be

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included in the perpendicular component. On the other hand, the bigger intensity of the fourth and sixth signals can be explained from the presence in the solution of a monomeric species originating from partial dissociation of the dimeric compound, as corroborated by comparing the title spectrum with the EPR spectrum of a much more diluted solution of complex I. The $\Delta M_s = \pm 2$ region shows seven hyperfine lines (average spacing 84 G), which supports the dimeric nature of the species.¹⁵ This behavior is similar to that reported by Haddad and Hendrickson for the $[\text{Cu}_2(\text{tren})_2(\text{Bilm})](\text{BPh}_4)$ complex.¹⁶ Furthermore, in the g_{\perp} component of the $\Delta M_s = \pm 1$ region can be observed the super-hyperfine structure consisting of 14 lines. Wieserma and Windle¹⁷ indicate that a CuN_3O chromophore should present seven signals according to the intensity ratios 1:3:6:7:6:3:1. In the present case, the weak resolution does not allow us to determine these ratios, but the existence of 14 signals suggests the presence of two CuN_3O chromophores in the dimer and confirms the deductions from the low-field and g_{\parallel} regions. The calculated A_{\parallel} value ($177 \times 10^{-4} \text{ cm}^{-1}$) is characteristic of a tetragonally distorted octahedral geometry around the $\text{Cu}(\text{II})$ ions.¹⁸

Table IV shows that the g parameters obtained for complex I on a polycrystalline sample and on a DMF saturated solution are different, suggesting that although a dimeric specie exists in solution, a change in the copper environment might have taken place. In fact, the vis d-d maximum suffers an hypsochromic shift from the solid to the solution, probably owing to the interaction of the solvent molecules with the metal ion.

Electronic Spectra. The UV-vis maxima of the four complexes are given in Table IV together with their assignments. The diffuse-reflectance spectra of the four compounds each display a broad d-d band characteristic of $\text{Cu}(\text{II})$ in a distorted octahedral environment. In the UV region, the $34\,364\text{-cm}^{-1}$ maximum of the free Acm^5 shifts to lower frequencies in complexes I-III, as a result of the deprotonation of Acm and the coordination to copper ion.

Besides the intraligand and d-d bands, the electronic spectrum of complex I exhibits a shoulder centered at about $27\,000 \text{ cm}^{-1}$. The origin of this band has been controversial.¹⁹⁻²³ It appears

to now be generally accepted that this band is a charge-transfer ligand to metal transition,²⁴⁻²⁶ which can be assigned to a $\pi\text{N}(\text{thiadiazole}) \rightarrow \text{d}$ charge transfer following detailed work of Fawcett²⁷ and Dagdigian.²⁸ Another possibility would be that the band corresponded to the $\sigma\text{N}(\text{sulfonamido}) \rightarrow \text{d}$ CT transition, but literature indicates that this band usually appears at higher frequencies.^{29,30}

Magnetic Susceptibility. Table IV shows the effective magnetic moment values (per Cu unit) for the four copper complexes at room temperature. The compounds I and II exhibit the usual magnetic moment for a d^9 ion, while the μ_{eff} of compounds III and IV suggest an antiferromagnetic coupling. The temperature dependence of molar powder magnetic susceptibility (χ_M) for compounds I and II indicates that there is no evidence of an exchange interaction down to 7.9 K. This behavior in the case of compound I is according to the molecular structure (see Figure 1), where the overlapping between the magnetic orbitals ($\text{d}_{x^2-y^2}$) is very weak.

A complete report on the magnetic behavior versus T of the other two copper compounds (III and IV) will be reported later, following the acquisition of a good data set at extremely low temperature.

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Supplementary Material Available: Tables S1-S6, listing physical properties and main data relating to the measurement and refinement of structure I, positional parameters, hydrogen atom coordinates, anisotropic thermal parameters, equations of least-squares planes, and hydrogen-bond distances, and Figures S1-S5, showing a stereoscopic view of the unit cell with the four discrete units of I and EPR powder spectra at room temperature and 110 K of complexes I-IV, respectively (10 pages); Table S7, listing observed and calculated structure factors (11 pages). Ordering information is given on any current masthead page.

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