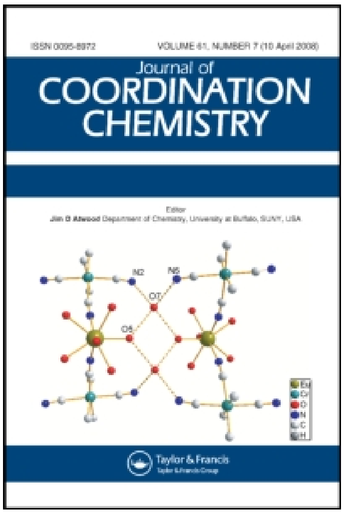


Journal of Coordination Chemistry
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713455674

EXPERIMENTAL PROOF OF THE EXISTENCE OF THE “HALF-UNIT” 7-AMINO-4-METHYL-5-AZA-3-HEPTENE-2-ONE (AEH). CRYSTAL STRUCTURE OF A NOVEL DIBROMO-BRIDGED DICOPPER(II) COMPLEX $(CuAEBr)_2$

Jean-Pierre Costes[a]; Francoise Dahan[a]; Jean-Pierre Laurent[a]
[a] Laboratoire de Chimie de Coordination du CNRS, associé a à l ' Université Paul Sabatier, Toulouse, France

To cite this Article Costes, Jean-Pierre , Dahan, Francoise and Laurent, Jean-Pierre(1984) 'EXPERIMENTAL PROOF OF THE EXISTENCE OF THE “HALF-UNIT” 7-AMINO-4-METHYL-5-AZA-3-HEPTENE-2-ONE (AEH). CRYSTAL STRUCTURE OF A NOVEL DIBROMO-BRIDGED DICOPPER(II) COMPLEX $(CuAEBr)_2$', Journal of Coordination Chemistry, 13: 4, 355 — 362

To link to this Article: DOI: 10.1080/00958978408073890

URL: http://dx.doi.org/10.1080/00958978408073890

J. Coord. Chem., 1984, Vol. 13, p. 355-362
0095-8972/84/1304-0355 $18.50/0

EXPERIMENTAL PROOF OF THE EXISTENCE OF THE "HALF-UNIT" 7-AMINO-4-METHYL-5-AZA-3-HEPTENE-2-ONE (AEH). CRYSTAL STRUCTURE OF A NOVEL DIBROMO-BRIDGED DICOPPER(II) COMPLEX $(CuAEBr)_2$

JEAN-PIERRE COSTES,[†] FRANCOISE DAHAN
and
JEAN-PIERRE LAURENT

Laboratoire de Chimie de Coordination du CNRS associé à l'Université Paul Sabatier, 205 route de Narbonne, 31400 Toulouse, France.

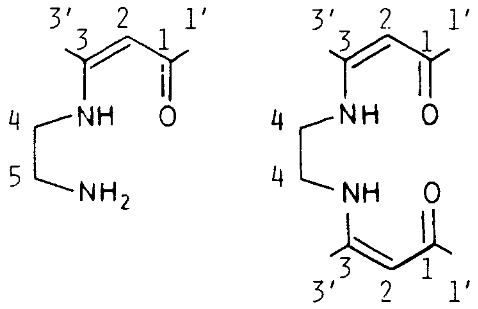
(Received March 21, 1984)

Under suitable conditions, the single condensation of acetylacetone with ethylenediamine may occur to yield a "half-unit", 7-amino-4-methyl-5-aza3-heptene-2-one (AEH), which has been characterized by ^1H and ^{13}C NMR. The existence of this ligand is definitively supported by a single-crystal X-ray structural analysis of di-μ-bromo-bis(7-amino-4-methyl-5-aza-3-heptene-2-onato)(1-)dicopper(II). EPR spectra give proof of spin-spin interactions between pairs of copper ions within dimers in the solid state and in solution. Low temperature spectra suggest that the interaction is antiferromagnetic.

INTRODUCTION

There are numerous accounts in the literature describing the chemistry of metal complexes of Schiff base ligands containing two, four, five and six donor atoms. Particular attention has been paid to complexes of tetradentate diimino bases such as *N,N'*-ethylene-bis(acetylacetoneimine) (abbreviated as $BAEH_2$ in the following) or *N,N'*-ethylene-bis(salicyl-ideneimine). These ligands result from the condensation of two molecules of the keto-precursor with one molecule of diamine. Very few of the ligands reported so far have arisen from the condensatio of the carbonyl function with only one end of the diamine. Generally speaking, they have been prepared by template synthesis and isolated as their metal complexes or by partial hydrolysis of symmetrical quadridentate[1,2,3,4] or quinquedentate Schiff bases. Furthermore, very few structural data are mentioned in the literature.[5,6,7] We have recently reported[8] the possibility of preparing a free Schiff base, 7-amino-4-methyl-5-aza-3-heptene-2-one [abbreviated as AEH in the following since it can be considered as the half-unit related to *N,N'*-ethylene-bis(acetylacetoneimine) usually abbreviated as $BAEH_2$; this analogy suggests for AEH, the trivial name of *N*-(acetylacetoneimine)ethylenediamine] from the single condensation of acetylacetone with ethylenediamine. According to its terdentate character, this ligand (*cf.* Figure 1) is expected to be readily involved in complexes belonging to the general type $M(AE)_2$. In the present paper we wish to describe a less common type, *i.e.*, Cu(AE)X. We succeeded in growing single crystals of the bromo derivative suitable for an X-ray diffraction study. The structural data support definitively the existence of AEH which has been previously deduced from solution studies. Furthermore, they show the complex to be a dimer involving pentacoordinated copper atoms.

[†] To whom correspondence should be addressed.



AEH BAEH$_2$

FIGURE 1 Ligand AEH.

EXPERIMENTAL

Microanalyses were carried out by the Service Central de Microanalyse du CNRS, Lyon. IR spectra in KBr discs were measured using a Perkin-Elmer 983 instrument. Electronic absorption and diffuse reflectance spectra were obtained by using a Cary 14 spectrophotometer. Proton and ^{13}C NMR spectra were run on a Bruker WH90. Measurements of electrolytic conductance were made with 10^{-3} M methanolic solutions. We obtained a value of 85 Ω^{-1} cm^2 mole^{-1} for the equivalent conductivity which fits well with the value expected for a 1:1 electrolyte in methanol (range 80-115 Ω^{-1} cm^2 mole^{-1}).[9]

Compound (CuAEBr)$_2$.

To a 2×10^{-3} mol dm^{-3} solution of AEH[8] in methanol was first added the equivalent amount of $LiOH.H_2O$ and, a few minutes later, a solution of $CuBr_2$ (2×10^{-3} mol dm^{-3}) in methanol. The solution turned blue upon stirring at room temperature for half an hour. After concentration of the solution, ether was added and the solution was quickly filtered to remove the inorganic salts. Concentration of the solution gave a blue-green powder. Found: C, 29.13; H, 4.70; N, 9.55; Br, 28.05; Cu, 22.20%. $C_7H_{13}BrCuN_2O$ requires C, 29.53; H, 4.57; N, 9.84; Br, 28.09; Cu, 22.32%. Slow crystallization from a dilute methanolic solution gave dark blue crystals suitable for X-ray diffraction study.

Collection and Reduction of X-ray Data.

Preliminary Weisenberg photographs indicated the crystal to be monoclinic, space groups $P2_1/c$ or $P2_1/n$. The structure was solved in the space group C_{2h}^5-$P2_1/n$. The selected crystal was a dark blue rhomb with boundary planes {010}, {101} and {10$\bar{1}$}. The distances from these faces to an arbitrary origin were 0.125, 0.162 and 0.138 mm, respectively. The crystal was sealed on a glass fiber and mounted on an Enraf-Nonius CAD4 diffractometer. Cell constants were obtained from a least-squares fit of the setting angles of 25 reflections. A summary of crystal and intensity collection data are given in Table I. A total of 2177 independent reflections were recorded to a 2θ(Mo) maximum of 54° by procedures described elsewhere.[10] Intensity standards, recorded periodically, showed only random, statistical fluctuations. Data reduction was then performed. Absorption corrections were made with use of the program AGNOST[11] (T_{min} = 0.103, T_{max} = 0.295). A total of 1582 reflections for which $Fo^2 > 4\sigma(Fo^2)$ were used in subsequent calculations.

TABLE I
Summary of crystal and intensity collection data.

Compound:	$(C_7H_{13}N_2OCuBr)_2$ 0.3 HBr
Formula:	$C_{14}H_{26.3}N_4O_2Cu_2Br_{2.3}$
Formula weight:	593.17 $a = 6.1707(6)$ Å $b = 13.045(2)$ Å $\beta = 102.237(6)°$ $c = 12.719(1)$ Å $V = 1000.6$ Å^3 $Z = 2$ $F(000) = 585.6$ $Dm = 1.96$ g/cm^3 (measured by flotation in CCl_4-C_2Br_4) $Dc = 1.969$ g/cm^3
Space group:	C_{2h}^5-$P2_1/n$
Radiation:	MoKα from graphite monochromator
Linear absorption coefficient:	$\mu = 67.0$ cm^{-1}
Temperature:	20°
Receiving aperture:	4.0 × 4.0 mm; 30 cm from crystal
Take-off angle:	3.45°
Scan mode:	θ-2θ
Scan range:	$(1.00 + 0.35 \tan\theta)°$
2θ limits:	54°

Structure Solution and Refinement.

The structure was solved[12] by the heavy-atom method. The Patterson map revealed the position of copper and bromine atoms. Subsequent Fourier maps revealed the positions of all non-hydrogen atoms of the monomeric asymmetric unit and the presence of a residual peak of 7e/Å^3 height related to itself centrosymmetrically (*ca.* 1.7 Å). This disordered atom was introduced as a bromine, Br†, and its occupancy factor was first allowed to vary and then kept fixed to 15% in the final cycles of refinement. All non-hydrogen atoms were refined anisotropically.

The hydrogen atoms were located on a difference Fourier map and introduced in calculations in idealized positions (C-H = N-H = 0.95 Å) with temperature factors kept fixed. A difference electron density map omitting the H(C4) atom was calculated to check the presence of this hydrogen peak. This peak is always present, half-way between C(4) and the disordered bromine Br†.

The atomic scattering factors used were those proposed by Cromer and Waber[13] with anomalous dispersion effects.[14] Scattering factors for the hydrogen atoms were taken from Stewart et al.[15]

The final full-matrix least-squares refinement converged to $R = \Sigma\,||Fo| - |Fc||/\Sigma\,|Fo| = 0.036$ and $R_w = [\Sigma w(Fo - Fc)^2/\Sigma w\,Fo^2]^{1/2} = 0.046$ with 1582 observations and 118 variables. The weighting scheme used in the minimization of the function $\Sigma w(Fo - Fc)^2$ was defined as $w = 1/[\sigma^2(Fo) + (0.044Fo)^2]$. An analysis of variance showed no unusual trends.

The final atomic coordinates and thermal parameters with their estimated standard deviations are given in Tables II and III. A list of observed and calculated structure factors (8 pp.) is available from the Editor on request.

TABLE II
Final least-squares atomic coordinates and anisotropic thermal parameters (Å^2 × 100) with estimated standard deviations in parentheses.

Atom	x/a	y/b	z/c	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
Cu	0.43634(8)	0.36749(4)	0.49928(4)	2.72(3)	3.29(3)	3.72(3)	0.18(2)	−0.47(2)	−0.65(2)
Br	0.39511(7)	0.48794(3)	0.64353(3)	3.63(3)	3.89(2)	3.88(3)	0.13(2)	0.29(2)	−0.75(2)
O	0.7291(5)	0.3309(2)	0.5732(2)	3.5(2)	3.5(2)	5.2(2)	0.7(1)	−1.0(1)	−0.8(1)
N(1)	0.3878(6)	0.2419(3)	0.4143(3)	3.6(2)	3.5(2)	3.3(2)	−0.7(2)	0.3(1)	−0.6(1)
C(1)	0.1695(7)	0.2410(4)	0.3393(3)	4.1(2)	5.0(3)	3.7(2)	−1.5(2)	−0.3(2)	−1.0(2)
C(2)	0.1038(8)	0.3498(4)	0.3122(4)	3.3(2)	5.6(3)	4.6(3)	0.4(2)	−0.8(2)	−0.5(2)
N(2)	0.1430(6)	0.4102(3)	0.4126(3)	3.0(2)	5.3(2)	4.6(2)	0.5(2)	−0.3(2)	−1.0(2)
C(3)	0.8210(7)	0.2436(3)	0.5650(3)	3.4(2)	3.6(2)	3.8(2)	0.6(2)	0.8(2)	1.0(2)
C(4)	0.7306(8)	0.1653(3)	0.4972(4)	4.7(3)	3.5(2)	4.8(3)	1.0(2)	1.0(2)	0.4(2)
C(5)	0.5208(8)	0.1643(3)	0.4236(3)	5.0(3)	3.0(2)	3.7(2)	−0.6(2)	1.2(2)	0.0(2)
C(6)	1.0435(7)	0.2297(4)	0.6381(4)	4.0(3)	5.5(3)	5.0(3)	1.4(2)	0.4(2)	1.0(2)
C(7)	0.4633(11)	0.0691(4)	0.3567(5)	9.4(5)	3.4(3)	6.3(3)	−0.4(3)	−0.0(3)	−1.2(2)
Br$^+$	0.9099(6)	0.0469(2)	0.5033(3)	5.8(2)	2.9(2)	8.4(3)	2.2(1)	2.6(2)	0.9(2)

TABLE III
Hydrogen atomic positional and thermal parameters (Å^2 × 100).

Atom	x/a	y/b	z/c	U
H1(C1)	0.179	0.205	0.276	4.6
H2(C1)	0.063	0.209	0.372	4.6
H1(C2)	−0.049	0.353	0.278	4.6
H2(C2)	0.190	0.377	0.265	4.6
H1(N2)	0.144	0.481	0.397	4.6
H2(N2)	0.030	0.397	0.451	4.6
H(C4)	0.834	0.111	0.503	4.6
H1(C6)	1.062	0.199	0.707	6.5
H2(C6)	1.090	0.299	0.646	6.5
H3(C6)	1.130	0.194	0.597	6.5
H1(C7)	0.581	0.021	0.375	9.0
H2(C7)	0.442	0.086	0.283	9.0
H3(C7)	0.331	0.040	0.370	9.0

RESULTS AND DISCUSSION

The reaction of pentane-2,4-dione with 1,2-diaminoethane generally yields the quadridentate Schiff base *N,N'*-ethylene-bis(acetylacetoneimine) (BAEH)$_2$. However, if the reaction is carried out with a 1:1 ratio of the reagents in carbon tetrachloride or chloroform and under dilute conditions, the "half-unit" AEH is formed. This reaction is formally similar to the reaction of (*o*-hydroxyphenyl)-butanedione with 1,2-di-aminopropane[16] to yield a single condensation product. However, the steric interaction, which is postulated to inhibit the formation of a double condensation product in the latter case, cannot be invoked in the case of AEH. In spite of a moderate stability at room temperature, AEH may be isolated with a reasonable degree of purity by vacuum distillation. Its NMR (^{1}H and ^{13}C) characteristics are reported in Table IV. They do not differ greatly from those of the corresponding quadridentate Schiff base BAEH$_2$. The most significant difference is related to the CH$_2$ groups of the diamino group which are equivalent in BAEH$_2$ and inequivalent in AEH as expected on the basis of its supposed structure (Figure 1).

Copper(II) complexes of AEH are prepared without difficulty. The reaction of AEH with CuBr$_2$ in the presence of LiOH gives complexes which, according to analytic data, have to be formulated as CuAEBr. This compound appears as a blue powder. Crystals

TABLE IV
^{1}H and ^{13}C chemical shifts[a] (ppm *vs* TMS) of 7-amino-4-methyl-5-aza-3-heptene-2-one (AEH) and *N,N'*-ethylene-bis(acetylacetoneimine) ($BAEH_2$).

		CH_3			CH_2	CH	CNH	C=O	NH_2
		1'	3'	4	5	2	3	1	
^{1}H	AEH	1.87	1.82	3.19(q)	2.76(t)	4.86	10.80	—	1.39
	$BAEH_2$	2.13	2.00	3.47(d+s)		4.98	11.4	—	—
^{13}C	AEH	27.4	17.5	45.5	40.8	94.0	162.1	193.1	—
	$BAEH_2$	28.6	18.4	43.4		95.9	162.7	195.3	—

[a](s) singlet; (d) doublet; (t) triplet; (q) quadruplet. J = 6Hz for (d), (t) and (q). Numbering of atoms as in Figure 1.

suitable for X-ray diffraction study have been obtained by careful recrystallisation from a dilute methanolic solution. However, the resulting crystals analyze as CuAEBr 0.15HBr. The presence of HBr may be due to traces of water in the solvent. It is worthy of note that dissolution of CuAEBr in methanol results in a large increase of the electrical conductivity consistent with the formation of an ionic species, $[CuAESolvent]^{+}Br^{-}$. This is further supported by spectroscopic (EPR, UV-visible) data (*vide infra*).

Description of the Structure of $(CuAEBr)_2$0.3HBr.

The complex consists of dimeric units which are well separated from each other. A view of the dimeric unit is given in Figure 2. The bridging Cu_2Br_2 core is constrained to be planar by the presence of a crystallographic inversion centre in the middle of the dimer. The relevant interatomic distances and angles are listed in Tables V and VI.

As can be seen in Figure 2 and from an examination of Tables V and VI, the geometry at each copper(II) center is a severely distorted tetragonal pyramid with the basal plane consisting of two nitrogen and one oxygen atoms from the AE ligand and a

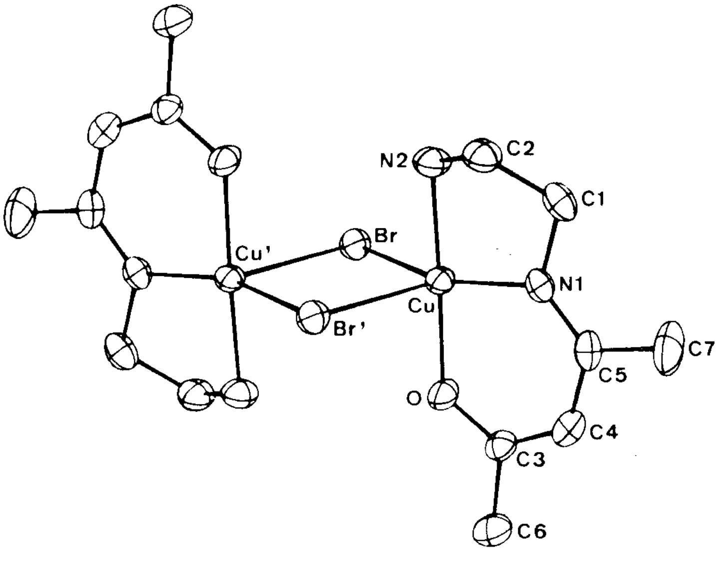


FIGURE 2 ORTEP Plot of the $[CuAEBr]_2$ dimer with thermal ellipsoids drawn at 40% probability level.

TABLE V
Copper atom environment: bond lengths (Å) and angles (°).

Cu-Br	2.4693(7)	Br-Cu-Br′	98.96(2)
Cu-Br′	2.9561(7)	Cu-Br-Cu′	81.04(2)
Cu-N(1)	1.951(3)	N(1)-Cu-N(2)	85.0(1)
Cu-N(2)	1.990(3)	N(1)-Cu-0	94.7(1)
Cu-0	1.912(3)	N(2)-Cu-0	175.2(2)
Br-Cu-N(1)	156.7(1)	Br′-Cu-N(1)	103.2(1)
Br-Cu-N(2)	90.5(1)	Br′-Cu-N(2)	83.0(1)
Br-Cu-0	91.6(1)	Br′-Cu-0	92.4(1)

TABLE VI
Bond lengths (Å) and angles (°).

N(1)-C(1)	1.477(5)	C(4)-C(5)	1.428(6)
C(1)-C(2)	1.496(7)	C(5)-N(1)	1.292(6)
N(2)-C(2)	1.476(6)	C(3)-C(6)	1.497(6)
O-C(3)	1.287(5)	C(5)-C(7)	1.505(6)
Cu-N(1)-C(1)	112.1(3)	O-C(3)-C(4)	125.5(4)
Cu-N(1)-C(5)	125.9(3)	O-C(3)-C(6)	114.7(4)
C(1)-N(1)-C(5)	121.8(3)	C(4)-C(3)-C(6)	119.7(4)
N(1)-C(1)-C(2)	107.8(4)	C(3)-C(4)-C(5)	127.5(4)
N(2)-C(2)-C(1)	108.7(4)	N(1)-C(5)-C(4)	121.5(4)
Cu-N(2)-C(2)	107.0(3)	N(1)-C(5)-C(7)	121.7(4)
Cu-O-C(3)	124.6(3)	C(4)-C(5)-C(7)	116.8(4)

bromine ion while the apical site is occupied by another bromine ion which is basal to the second copper atom in the dimer. The distortions from the ideal square-pyramidal (SP) geometry are important but less considerable than those related to trigonal bipyramidal (TBP) geometry. For instance, the *trans* O-Cu-N(2) angle is 175.2(2)° which is a typical value for tetragonal pyramidal complexes but the *trans* Br-Cu-N(1) angle is only 156.7(1)°. Furthermore the four basal atoms deviate markedly from coplanarity with O and N(2) being 0.234(3) and 0.373(4) Å above the mean plane, respectively, while Br and N(1) are 0.0036(4) and 0.348(3) Å below the plane, respectively. The copper atom lies out of this plane by 0.2257(5) Å in the direction of the Br' apical atom, a condition which seems characteristic of five-coordinated copper(II) complexes. The copper atom also lies out of the N(1), Br, Br′ plane by 0.1208(5) Å and the equatorial angles Br′-Cu-N(1), Br-Cu-N(1) and Br-Cu-Br′ of 103.2(1)°, 156.7(1)°, and 98.96(2)°, respectively., deviate considerably from the ideal value of 120° for trigonal bipyramidal geometry.

The Cu-N distances of 1.951(3) and 1.990(3) Å and the Cu-O distance of 1.912(3) Å are within the range of values normally observed for such bonds. More particularly, they are almost identical with those reported for *N,N′*-ethylenebis(acetylacetoneiminato)copper(II).[17] Furthermore, the acetylacetone ring is planar with no atom deviating from the least-squares plane by more than 0.05 Å , with the copper atom lying only 0.0012(5) Å out of this plane. On the other hand, the five-membered ring defined by the copper atom and the ethylenediamine is definitely non-planar, with distortions more pronounced than those observed for $BAEH_2$. In both cases, this ring has a *gauche* conformation.

A relevant structural element is the quadrangle defined by the CuBrCu′Br′ core. The geometry of this bridging unit is compared with that observed in related dimeric bromo complexes in Table VII. The $(CuAEBr)_2$ complex is characterized by a low value of the Cu-Br′-Cu bridging angle whereas the out-of-plane Cu-Br′ distance of 2.956(1) Å is intermediate between the quoted values which range from 2.868 to 3.872 Å . These two features result in a short Cu-Cu′ separation of 3.5445(7) Å .

TABLE VII
Bond lengths (Å) and angles (°) in related compounds.

Complex[a]	Cu-Br in-plane	Cu-Br out-of-plane	Cu-Cu′	Cu-Br′-Cu	Ref.
$[Cu(DMG)Br_2]_2$	2.387	2.883	3.599	85.59	18
$[Cu(dmen)Br_2]_2$		2.868	3.570	83.71	19
$[Cu(2\text{-}pic)_2Br_2]_2$		3.872	4.926	100.4	20
$[Cu(4\text{-}Metz)_2Br_2]_2$		3.033	4.063	94.16	21
$[Cu(C_6H_8N_2)Br_2]_2$	2.385 2.422	3.260	3.737	80.77	22
$[CuAEBr]_2$	2.469	2.956	3.545	81.04	this work

[a] Ligand abbreviations: DMG = dimethylglyoxime; dmen = *N,N*-dimethylenediamine, 2-pic = 2-methylpyridine; 4-Metz = 4-methylthiazole.

Spectroscopic Data.

Regarding the infrared spectrum, we note the occurrence of two bands at 3270 and 3320 cm^{-1} which are attributed to the NH_2 group. Three bands at 1600, 1570 and 1515 cm^{-1} are assigned to $\nu_{C=O}$, $\nu_{C=C}$ and $\nu_{C=N}$. The band at 1600 cm^{-1} which does not appear in the spectrum of [5,7,12,14-tetramethyl-1,4,8,11-tetraazacyclotetradeca-4,6,11,12-tetraenato](2-)nickel(II) can be confidently attributed to $\nu_{C=O}$.[23]

Although the electronic spectra of copper(II) complexes do not generally provide valuable information on geometry, a criterion for distinguishing between trigonal bipyramidal (TBP) geometry and square pyramidal (SP) geometry has been proposed.[24] An absorption band in the 550-670 nm region is suggested to be indicative of SP geometry whereas an absorption in the 800-850 nm region is supposedly characteristic of TBP geometry. This generalization would imply that $(CuAEBr)_2$ which displays an absorption at 650 nm has a SP geometry.

The X-band EPR spectrum of a powdered sample shows an intense absorption at about 3120 G and a very weak signal at *ca* 1500 G, the latter being assigned to a $\Delta M_S = 2$ transition of a typical triplet species. This "half-field" transition is easily observed in frozen (CH_2Cl_2 + $CH_3C_6H_5$) solutions together with a broad unsymmetrical band which lies in the range 1800-3500 G and a weak, broad absorption centered at about 4100 G. A sharp intense line at 3370 G is likely attributable to a mononuclear species. Indeed at very low temperature (*ca* 5 K), this signal is almost the only feature discernible in the spectrum. Addition of methanol to the solvent mixture causes the observation of a well-resolved spectrum of the so-called tetragonal pattern with $g_{//} = 2.243$, $A_{//} = 200$ G and $g = 2.044$. Five lines are clearly resolved in the perpendicular signal with a spacing of 11 G suggesting an interaction of the unpaired spin with two nitrogen nuclei.

Assignment of resonance fields in the triplet spectrum is made impossible by the broadening of the spectrum and the presence of signals related to a mononuclear species. From the position of the "half-field" transition and by making use of Kottis-Lefebvre's formula,[25] the zero-field splitting parameter is evaluated, $D_{//} \cong 1250$ G. From the absence of a triplet signal at low temperature, it may be concluded that an antiferromagnetic interaction is operative.

Finally, it is clear that the dimeric structure is retained in non-coordinating solvents leading to the observation of a triplet spectrum. In methanol, a coordinating solvent, the dimer dissociates. The observation of superhyperfine structure on the perpendicular g signal suggests that the AE ligand remains coordinated to the metal. The electronic spectrum of this solution with respect to that of a solid sample is extremely altered. Two absorptions are detected; one at 615 nm ($\varepsilon \cong 75$) and one as a shoulder at 430 nm ($\varepsilon \cong 70$) near the charge transfer bands. These two observations are consistent with square planar geometry. Furthermore, the conductivity data in methanol given in the experimental section fit well with a 1:1 electrolyte. Thus, it seems likely that breaking of Cu-Br bonds and entry of a solvent molecule into the copper(II) coordination sphere has occurred.

REFERENCES

1. R.C. Elder, *Aust. J. Chem.*, **31,** 35 (1978).
2. H.A. Goodwin and F. Lions, *J. Amer. Chem. Soc.*, **82,** 5013 (1960).
3. A.C. Braithwaite, C.E.F. Rickard and T.N. Waters, *J. Chem. Soc., Dalton Trans.*, 2149 (1975).
4. W.N. Wallis and S.C. Cummings, *Inorg. Chem.*, **13,** 991 (1974).
5. P.G. Beckingsale, A.T. Morcom, C.E.F. Rickard and T.N. Waters, *J. Chem. Soc., Dalton Trans.*, 2135 (1977).
6. A.P. Summerton, A.A. Diamantis and M.R. Snow, *Inorg. Chim. Acta*, **27,** 123 (1978).
7. H. Adams, N.A. Bailey, J.-P. Costes, D.E. Fenton and J.R. Tate, International Conference on Inorganic Stereochemistry, Reading, England, Poster A25, 1982.
8. J.-P. Costes and G. Cros, *C.R. Acad. Sci.*, **294-II,** 173 (1982).
9. W.J. Geary, *Coord. Chem. Rev.*, **7,** 81 (1971).
10. A. Mosset, J.-J. Bonnet and J. Galy, *Acta Cryst.*, **B33,** 2639 (1977).
11. P. Coppens, L. Leiserowitz and D. Rabinovitch, *Acta Cryst.*, **18,** 1035 (1965).
12. G.M. Sheldrick, Shelx 76, Program for crystal structure determination; University of Cambridge, Cambridge, England (1976).
13. D.T. Cromer and J.T. Waber, "International Tables for X-ray Crystallography", Vol. IV, Table 2.2 A, pp. 72–79, Kynoch Press, Birmingham, England, 1974.
14. D.T. Cromer, *ibid.* ref. 13, Table 2.3.1, p. 149.
15. R.F. Stewart, E.R. Davidson and W.T. Simpson, *J. Chem. Phys.*, **42,** 3175 (1965).
16. G. Bett, D.E. Fenton and J.R. Tate, *Inorg. Chim. Acta*, **54,** 2101 (1981).
17. D. Hall, A.D. Rae and T.N. Waters, *J. Chem. Soc.*, 5897 (1963).
18. H. Endres, *Acta Cryst.*, **B34,** 3736 (1978); M. Megnamisi-Belombe and M.A. Novotny, *Inorg. Chem.*, **19,** 2476 (1980).
19. D.W. Phelps, W.H. Goodman and D.J. Hodgson, *Inorg. Chem.*, **15,** 2266 (1976).
20. P. Singh, D.Y. Jeter, W.E. Hatfield and D.J. Hodgson, *Inorg. Chem.*, **11,** 1657 (1972); D.Y. Jeter, D.J. Hodgson and W.E. Hatfield, *Inorg. Chim. Acta*, **5,** 257 (1971).
21. W.E. Marsh, T.L. Bowman, C.S. Harris, W.E. Hatfield and D.J. Hodgson, *Inorg. Chem.*, **20,** 3864 (1981).
22. H.M. Helis, W.H. Goodman, R.B. Wilson, J.A. Morgan and D.J. Hodgson, *Inorg. Chem.*, **16,** 2412 (1977).
23. J.-P. Costes, unpublished data.
24. B.J. Hathaway and A.A.G. Tomlinson, *Coord. Chem. Rev.*, **5,** 1 (1970).
25. P. Kottis and R. Lefebvre, *J. Chem. Phys.*, **39,** 393 (1963).