sequently, this novel hydrogen bonding system could be regarded as a significant driving force to the spontaneous fixation of CO_2 under atmospheric conditions.

As to the solution-phase structure of complex **2**, whether the hydrogen bonding system was retained or not was not yet clear.

Examinations with Other *N*-Alkyl-Substituted Diamines. Analogous diamines were examined to elucidate the N-substituent effect on the CO_2 uptake. When *N*-methylethylenediamine, *N*-ethylethylenediamine, and *N*,*N*-diethylethylenediamine were used as the diamine part, no fixation of CO_2 in air was observed. *N*-Methylethylenediamine and *N*-ethylethylenediamine were likely to form tris(diamine)nickel(II) complexes, and *N*,*N*-diethylethylenediamine led to precipitation of a bis(diamine) square-planar nickel(II) complex. Further, *N*,*N'*-dimethylethylenediamine (*N*,*N'*-Me_2en), which forms preferably *trans*-(*O*,*O*)-$[Ni(N,N'\text{-}Me_2en)_2(H_2O)_2]^{2+}$ in an aqueous medium, failed to adsorb CO_2 in air. This is probably due to the instability of the *cis*-(*O*,*O*)-$[Ni(N,N'\text{-}Me_2en)_2(H_2O)_2]^{2+}$ unit. Thus, the N-substituents of ethylenediamine dramatically influenced the present system, and the spontaneous fixation of CO_2 is unique to the nickel(II)–*N*,*N*-Me_2en system.

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Supplementary Material Available: Listings of crystallographic data, positional and anisotropic thermal parameters, atomic parameters of hydrogen atoms, and bond distances and bond angles and a figure showing crystal packing (12 pages); a table of structure factor amplitudes (14 pages). Ordering information is given on any current masthead page.

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Crystal Structure and Spectroscopic Properties of a Novel Mixed-Valence Compound Containing Tetrabromocuprate(II) and Tribromocuprate(I) Anions

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The preparation, crystal structure, electronic and ESR spectra are reported for the mixed valence Cu(II)/Cu(I) compound $[LH_3]_4[CuBr_3][CuBr_4]\cdot H_2O\cdot 3CH_3OH$ (where LH_2 = 6-amino-1,3-dimethyl-5-((2-carboxyphenyl)azo)uracil). The compound crystallizes in the triclinic space group $P1$ with a = 15.069 (5), b = 16.207 (7), c = 16.519 (5) Å, α = 90.50 (3), β = 107.67 (3), γ = 105.40 (3)°, Z = 2, R = 0.089, and R_w = 0.068. The $[CuBr_4]^{2-}$ anion shows a distorted tetrahedral geometry with bond lengths in the range 2.340 (4)–2.396 (3) Å and angles of two types, 125.7 (2)–133.0 (2)° and 98.4 (1)–101.8 (1)°. The $[CuBr_3]^{2-}$ anion has a planar triangular geometry with very approximate C_{2v} symmetry. The bond lengths and angles are in the ranges 2.347 (4)–2.398 (4) Å and 117.4 (2)–123.9 (1)°, respectively. Intermolecular distances between the ions and solvent molecules suggest extensive hydrogen bonding network.

Introduction

6-Amino-1,3-dimethyl-5((2-carboxyphenyl)azo)uracil (hereafter denoted as LH_2) can coordinate to metal ions as a bidentate, a tridentate, and a tetradentate ligand, yielding mononuclear, dinuclear and tetranuclear metal complexes, respectively, which present interesting magnetic properties.[1-3] We have recently reported a tetranuclear compound $[Cu_4(L)_3(LH)(NO_3)(H_2O)]\cdot 2H_2O$ having a quasi-tetrahedral arrangement of the four copper(II) atoms and a ferromagnetic ground state.[3] In an attempt to prepare new tetranuclear complexes of this type, a compound having the formula $Cu_2Br_7(LH_3)_4\cdot H_2O\cdot 3CH_3OH$ was obtained. The present paper is devoted to the structural and spectroscopic studies of this compound, which have revealed that $Cu_2Br_7(LH_3)_4\cdot H_2O\cdot 3CH_3OH$ is a mixed-valence Cu(II)/Cu(I) compound containing $[CuBr_4]^{2-}$ and $[CuBr_3]^{2-}$ anions. Compounds having a metal in two valence states are of special interest because of the possibility of electron transfer between these states, which is of great importance in a large range of chemical and biochemical catalytic systems.[4] Cu(II)/Cu(I) compounds present an additional interest, because of different coordination numbers and stereochemistry adopted by Cu(II) and Cu(I); both oxidation states are labile and stereochemically flexible. From these reasons, the chemistry of mixed-valence Cu(II)/Cu(I) compounds has received considerable attention in the last few years. Thus, a number of these compounds has been prepared and their structures determined by X-ray diffraction methods.[5]

Table I. Crystallographic Data for $[LH_3]_4[CuBr_3][CuBr_4]\cdot H_2O\cdot 3CH_3OH$

chem formula: $C_{55}H_{68}Cu_2Br_7N_{20}O_{20}$	chem formula: $C_{55}H_{68}Cu_2Br_7N_{20}O_{20}$
a = 15.069 (5) Å	fw = 2015.70
b = 16.207 (7) Å	space group: $P1$ (No. 2)
c = 15.519 (5) Å	T = 23–25 °C
α = 90.50 (3)°	λ = 0.71069
β = 107.67 (3)°	ρ_{calcd} = 1.82 g cm^{-3}
γ = 105.40 (3)°	R = 0.089
V = 3688 (2) Å^3	R_w[a] = 0.069
Z = 2	

[a] The function minimized with $R_w(|F_o| - |F_c|)^2$, where $w = 1/\sigma^2(F_o)$.

Experimental Section

Synthesis. LH_2 was synthesized by coupling diazotized anthranilic acid with 6-amino-1,3-dimethyluracil, according to the method described by Lythgoe et al.[6] The compound was recrystallized from hot pyridine

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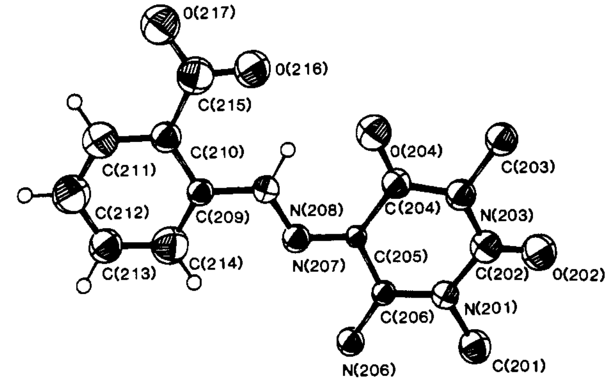

Figure 1. Configuration of the cations. Cation 2 with the labeling scheme is shown. The first digit of an atom refers to the cation number. The hydrogens connected to the methyl carbons are missing. The thermal ellipsoids in the ORTEP drawing for the non-hydrogen atoms are presented at the 50% probability level.

with a yield of 85%, mp 280–281 °C. The hydrobromide of the ligand, LH_3Br, was prepared by dissolving LH_2 in ethanol containing HBr in molecular ratio of 1:1. By slow evaporation of the solution at room temperature, yellow needles of the compound were obtained.

The compound $Cu_2Br_7(LH_3)_4\cdot H_2O\cdot 3CH_3OH$ was prepared by adding $CuBr_2$ (2.23 g, 10 mmol) to a solution of LH_3Br (0.384 g, 1 mmol) in methanol. The mixture was stirred for 30 min, and the resulting black homogeneous solution was allowed to stand at room temperature for 2 days, whereupon almost opaque crystals with metallic luster separated. They were filtered off, washed with methanol, and air-dried (yield: 68%). Anal. Calcd for $Cu_2Br_7C_{55}H_{68}N_{20}O_{20}$: C, 32.74; H, 3.50; N, 13.88; Cu, 6.30. Found: C, 33.22; H, 3.43; N, 13.66; Cu, 6.45.

Physical Measurements. Microanalyses of C, H, and N and IR spectra were performed as already described.[2] Copper was determined thermogravimetrically as CuO. The ESR spectra of the powdered Cu(II)/Cu(I) compounds were recorded at X-band frequencies with a Bruker 200TT spectrometer operating at 9.4–9.5 GHz, at room temperature and 90 K. The reflectance diffuse spectrum was recorded in the range 300–1400 nm using a Schimadzu MPC-3100 spectrophotometer.

Crystal Data Collection. A suitable deep violet, almost opaque single crystal was picked up after inspection with a polarizing microscope. Lattice parameters of the crystal were obtained from 25 high-angle reflections measured on a Nicolet P3 four-circle diffractometer. Crystal data, details of the data collection, and structure refinement information are given in Table I and in supplementary Table S1. The unique data set was measured within the specified 2θ limits in conventional ω-scan mode at ambient temperature. Intensities of three check reflections measured during the data collection after every 57 reflections showed only statistical variation. The data were corrected for Lorentz and polarization effects and for dispersion.

Solution and Refinement of the Structure. The structure was solved by direct methods.[7] Owing to the lack of statistically significant reflections, in the block-diagonal refinement anisotropic thermal parameters were assigned only to the copper and bromine atoms, while the other non-hydrogen atoms were refined isotropically. One of the three methanol molecules is disordered with the oxygen atom occupying two positions. The hydrogen atoms could not be reliably located from the difference Fourier maps. The aromatic hydrogens were placed at their fixed positions (C–H = 1.0 Å). A careful examination of the thermal parameters and bond lengths of the relevant atoms indicated the similar orientation of the four substituted uracil groups of $[LH_3]^+$ cations (Figure 1). Moreover, the two short N(6)–Br contacts of each cation confirmed further this assumption (Figure 2).

The distinction between the carbonyl and hydroxyl oxygen of the four carbonyl groups could be deduced from the comparison of the respective C–O bond lengths of each group (c.f. supplementary Table IV). In addition, in cations II, III, and IV intermolecular contacts to O(17) corroborated our choice. The oxygen atoms O(16) do not have any short intermolecular hydrogen bond contacts.

The extra proton necessary to achieve the positive charge was placed in each cation on the azo nitrogens N(8); N–H = 1.0 Å. The nitrogens N(7) do not show any short possible hydrogen bond contacts. Instead, the short N(8)–O(4) and N(8)–O(16) contacts (2.61–2.67 Å; see supplementary Table IV) enable the proton to participate in bifurcated hydrogen bonding between the atoms. In 6-amino-1,3-dimethyl-5-((2-ethylphenyl)azonium)uracil bromide dihydrate and 6-amino-1,3-dimethyl-5-(phenylazonium)uracil dichloroaurate(I) sesquihydrate the azo group is protonated instead of the amino group of the uracil ring.[8,9] All structure refinements were done by the XTAL program package,[10] and neutral atom scattering factors were those in the program.

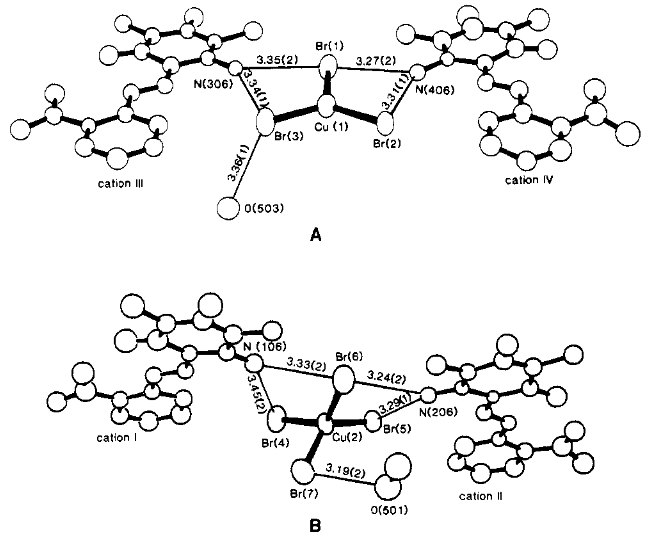

Figure 2. Bromocuprate anions with possible intermolecular interactions.

Results and Discussion

A deep violet crystalline compound having the stoichiometry $Cu_2Br_7(LH_3)_4\cdot H_2O\cdot 3CH_3OH$ has been obtained in the reaction of the hydrobromide of 6-amino-1,3-dimethyl-5-((2-carboxyphenyl)azo)uracil and a large excess of $CuBr_2$ in methanol solution.

The IR spectrum of the compound shows two bands due to ν(OH) of the water molecule at 3571 and 3473 cm^{-1}. The N=N stretching band of LH_2 occurring at 1524 cm^{-1} is shifted to 1440 cm^{-1}, indicating the protonation of LH_2 at the nitrogen atom of the azo group bonded to the phenyl ring.[8,9,11] Formation of relatively strong hydrogen bonding is consistent with the broad bands in the range 2400–3100 cm^{-1} due to ν(N–H) and ν(O–H).

The nonsilent ESR spectrum of the compound indicates that both copper atoms can not have oxidation state +1. On the other hand, it is very unlikely that both copper atoms have oxidation state +2, since one of them displays a coordination number of 3 and, to the best of our knowledge, no monomeric Cu(II) compounds of coordination numbers 3 have been reported. In view of IR data, the LH_2 molecules exist as monovalent cations with neutral carboxylic acid groups, which is further supported by the similarity of the geometry of the four LH_3^+ ions. From the stoichiometry of the compound, it is inferred that half of the copper ions have to be present in the univalent state and the other half in the bivalent state.

The reduction process of Cu(II) to Cu(I) has been also observed in the reaction of the $CuBr_2$/HBr mixture with tris(1-pyrazolylethyl)amine[12] or aminopyridines.[13] In the latter reaction, halogenation of the pyridine ring was shown to occur. It has been proposed that the reaction involves the reduction of copper(II) to copper(I) during the halogenation process. In the present case, the isolated compound does not contain a brominated aryl ring (see below); therefore, it is not possible to tie the existence of the Cu(I) to the bromination process. Indeed, as it has been pointed

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Table II. Positional Parameters with Their Standard Deviations for the Anions

atom	x	y	z	U_{eq},[a] Å^2
Cu(1)	0.2978 (2)	0.0725 (2)	0.6364 (2)	64 (2)
Cu(2)	0.0377 (2)	0.4166 (2)	0.1875 (2)	48 (2)
Br(1)	0.1868 (2)	−0.0293 (2)	0.5199 (2)	65 (2)
Br(2)	0.4521 (2)	0.1433 (2)	0.6286 (2)	57 (2)
Br(3)	0.2413 (2)	0.1007 (2)	0.7488 (2)	68 (2)
Br(4)	0.1697 (2)	0.5296 (2)	0.1829 (2)	73 (2)
Br(5)	−0.0363 (2)	0.4853 (2)	0.2642 (2)	54 (2)
Br(6)	−0.0979 (2)	0.3436 (2)	0.0671 (2)	87 (2)
Br(7)	0.1185 (2)	0.3073 (2)	0.2191 (2)	73 (2)

[a] The U_{eq} values for the Cu and Br atoms have been calculated as $U_{eq} = (1000/3)(U_{11} + U_{22} + U_{33})$.

Table III. Bond Lengths (Å) and Angles deg for the $[CuBr_3]^{2-}$ and $[CuBr_4]^{2-}$ Anions

	Bond Lengths		
Cu(1)–Br(1)	2.398 (4)	Cu(1)–Br(3)	2.353 (5)
Cu(1)–Br(2)	2.347 (4)		
Cu(2)–Br(4)	2.340 (4)	Cu(2)–Br(6)	2.396 (3)
Cu(2)–Br(5)	2.361 (5)	Cu(2)–Br(7)	2.381 (5)
	Bond Angles		
Br(1)–Cu(1)–Br(2)	118.6 (2)	Br(2)–Cu(1)–Br(3)	123.9 (1)
Br(1)–Cu(1)–Br(3)	117.4 (2)		
Br(4)–Cu(2)–Br(5)	101.8 (1)	Br(5)–Cu(2)–Br(6)	101.8 (1)
Br(4)–Cu(2)–Br(6)	125.7 (2)	Br(5)–Cu(2)–Br(7)	133.0 (2)
Br(4)–Cu(2)–Br(7)	98.4 (1)	Br(6)–Cu(2)–Br(7)	99.9 (2)

Table VI. Distortion from Regular Tetrahedral Geometry for $[CuBr_4]^{2-}$ Complexes

compound[a]	ΔD,[b] %	HB[c]	2θ,[d] deg	ref
$[NBHPAZH_2][CuBr_4]$	7.9	yes	118.9	18
$[H_2bim]_2[CuBr_4]$	9.5	yes	120.8	19
$[TMA]_2[CuBr_4]$	13.8	no	125.0	20
$[Cu(17\text{-}aneN_5)][CuBr_4]$	15.0	probably	126.0	21
$[LH_3]_4[CuBr_4][CuBr_3]\cdot H_2O\cdot 3CH_3OH$	18.5	yes	128.8	this work
$[enH_2]_2[CuBr_4]$	18.7	yes	129.6	22
$Cs_2[CuBr_4]$	19.7	no	128.4	23
$[ABMPyH][AMPyH]\text{-}[CuBr_4]$	21.0	yes	131.3	24
$[DIPA]_2[CuBr_4]$	21.2	yes	135.0	25
$[TMP]_2[CuBr_4]$	22.9	no	133.2	26
$[TMP]_2[CuBr_4]$[e]	23.0	no	132.6	26
$[ACMPyH]_2[CuBr_4]$	27.8	yes	137.1	17
$[MPEA]_2[CuBr_4]$	34.3	yes	142.1	18

[a] Key: $NBHPAZH_2$, *N*-phenylpiperidinium; H_2bim, benzimidazolium; TMA, tetramethylammonium; 17-aneN_5, 1,4,7,11,14-pentaazacycloheptadecane; enH_2, ethylenediammonium; ABMPyH, 2-amino-5-bromo-3-methylpyridinium; AMPyH, 2-amino-3-methylpyridinium; DIPA, diisopropylammonium; TMP, tetramethylphosphonium; ACMPyH, 2-amino-5-methylpyridinium; MPEA, methyl(phenylethyl)ammonium. [b] ΔD (dihedral distortion) was calculated according to

$$\Delta D = \frac{1}{n} \sum_j \frac{|\sum_i(\delta_i - \delta_{j1})|}{|(\delta_{j1} - \delta_{j2})|} \times 100$$

where δ_i is experimental dihedral angle, δ_{j1} is the theoretical dihedral angle for T_d, and δ_{j2} is theoretical dihedral angle for D_{4h}. [c] HB = hydrogen bonding. [d] 2θ is the mean value of the two largest Br–Cu–Br angles. [e] The compound contains two crystallographically independent $[CuBr_4]^{2-}$ anions in the unit cell.

out,[13] the Cu(I) ion may be generated by a reaction involving the decomposition of $CuBr_2$ to CuBr and Br_2. The large excess of $CuBr_2$ used in the preparation of the compound might contribute to this.

As the stoichiometry of the $Cu_2Br_7(LH_3)_4\cdot H_2O\cdot 3CH_3OH$ compound seems to indicate a complicated structure involving both copper(II) and copper(I), an X-ray diffraction study on the compound was undertaken. The results of the crystal structure determination confirm the ionic structure with a bulky asymmetric unit. The unit consists of two different bromocuprate anions, $[CuBr_3]^{2-}$ and $[CuBr_4]^{2-}$, four essentially similar, approximately coplanar $[LH_3]^+$ cations, three methanol molecules, and one crystal water molecule. The distances given in supplementary Table VIII suggest that the ions and the solvent molecules are bonded together by hydrogen bonds. There is no important interaction between bromocuprate anions, the shortest distance being 5.861 (5) Å, between Cu(2) and Br(6).

The configuration of a $[LH_3]^+$ cation and the bromocuprate anions with possible hydrogen bonds are shown in Figures 1 and 2 together with the atom labeling. The atomic coordinates of the $[CuBr_4]^{2-}$ and $[CuBr_3]^{2-}$ anions are listed in Table II and their bond lengths and angles in Table III. The atomic coordinates of the four independent $[LH_3]^+$ molecules are given in supplementary Table SII and their selected bond lengths and angles and intramolecular hydrogen bond contacts, including mean values of the four sets of bonds, are listed in supplementary Table IV.

As expected, the $[CuBr_4]^{2-}$ anion shows a distorted tetrahedral geometry. The Cu–Br bond lengths are in the range 2.340 (4)–2.396 (3) Å, being similar to those usually found for analogous compounds. The Br–Cu–Br bond angles vary within the range 98.4 (1)–133.0 (2)° showing that the geometry is intermediate between square planar (D_{4h}) and regular tetrahedral (T_d). To obtain a quantitative description, we will consider the procedure proposed by Muetterties,[14] which leads to a measure of polytopal shape referenced to idealized geometries, namely D_{4h} and T_d in the present case (Table V, supplementary material). The value ΔD = 18.5% indicates that the anion is not distorted much from regular tetrahedral geometry. This value and those observed for analogous compounds (Table VI), are in good accordance with the semiempirical MO study of the T_d–D_{4h} equilibrium in tetrabromometal complexes,[15] which indicates that the $[CuBr_4]^{2-}$ anion has a tendency to display the T_d configuration. Recently, using a vibronic coupling model, it has been demonstrated that the Jahn–Teller coupling is rather larger for Cu(II) in tetrahedral coordination ($^2T_2$ orbitally degenerated ground state) and generally dominates over steric ligands, geometric packing, or the spin–orbit effect, leading to a compressed tetrahedral configuration with D_{2d} symmetry.[16] In spite of these, no strict D_{2d} symmetry is usually found for $[CuBr_4]^{2-}$. The observed deviation from this symmetry is frequently or at least partly, due to nonelectronic effects, such as hydrogen bonding, van der Waals contacts, and host–lattice-induced distortions. In the present case, there are possibilities for extensive hydrogen bonds involving the bromine atoms which might force the $[CuBr_4]^{2-}$ anion to deviate from D_{2d} symmetry, affecting Cu–Br bond lengths and Br–Cu–Br angles.

It has been proposed that strong hydrogen bonding interactions favor a planar geometry in the $[CuBr_4]^{2-}$ anion.[17] However, as shown in Table VI, the distortion values for the $[CuBr_4]^{2-}$ anion in the present compound, $[NBHPAZH_2][CuBr_4]$,[18] and $[H_2bim][CuBr_4]$,[19] all of them with hydrogen bonds involving bromine atoms, are among the smallest observed. These observations are in contrast with the supposition above. Moreover, one

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of the compounds with no hydrogen bonds has a distortion value among the highest found. Accordingly, we may conclude that distortion from the T_d geometry is a result of the combined action of packing and large electronic effects. Thus the hydrogen bonding can act in concert with the electronic effects or to the opposite direction leading to either increase or decrease of the distortion from the T_d geometry. On the other hand, square-planar $[CuBr_4]^{2-}$ anions have been found only in compounds of the type M_2CuBr_4 (where M is an alkali-metal ion or monosubstituted ammonium ion) and $LCuBr_4$ (where L is a relatively small alkyldiammonium dication).[27] Yet, the Cu atom is not truly four-coordinate, since the structures consist of layers of square-planar $[CuBr_4]^{2-}$ anions linked together by semicoordinative Cu–Br bonds with the latter completing the Jahn–Teller elongated octahedral coordination geometry for the Cu(II) ions. Obviously, the size of the cation is an important factor affecting the type of the bromocuprate(II) anion. Thus, instead of two dimensional layers, few relatively small $[CuBr_6]^{2-}$ and $[Cu_3Br_8]^{2-}$ anions[28,29] and more commonly discrete $[CuBr_4]^{2-}$ anions are found in compounds containing large cations, as in the present structure.

The $[CuBr_3]^{2-}$ ion has a planar triangular geometry. The ion does not possess strict 3-fold symmetry since the Cu–Br bond lengths and Br–Cu–Br bond angles are not all equivalent, and it can be better considered to have approximately C_{2v} symmetry. The geometry of $[CuBr_3]^{2-}$ is quite similar to that observed for this anion in the following compounds: $[CuBr(TPyEA)_3]_3$-$[CuBr_3]Br\cdot 3H_2O$ (where TPyEA = tris((1-pyrazolylethyl)-amine),[12] bis(tetramethylphosphonium) tribromocuprate(I),[30] bis(3,5-dimethyl-1,2-dithiolium) tribromocuprate(I),[31] and bis-(methyltriphenylphosphonium) tribromocuprate(I).[32] To the best of our knowledge, the aforementioned compounds are the only examples so far reported of structurally characterized $[CuBr_3]^{2-}$ anions. Recently, the coordination number of copper(I) in the bromocuprate(I) anions has been correlated with the size of the cation,[30] so that large cations favor the formation of small, discrete anions, in which copper(I) exhibits a low coordination number. The structure of $[LH_3]_4[CuBr_4][CuBr_3]\cdot H_2O\cdot 3CH_3OH$ is a good example of this.

The far-IR spectrum shows bands due to ν(Cu–Br) at 250, 226, and 211 cm^{-1}. In good accord with the X-ray results, the position of the two former bands are similar to those observed for the E vibration mode in $[CuBr_4]^{2-}$ anions with nearly D_{2d} symmetry.[33] The latter band might be assigned to the E mode of the $[CuBr_3]^{2-}$ anion.[34]

The axial ESR spectrum of the solid compound is consistent with the compressed tetrahedral stereochemistry of the $[CuBr_4]^{2-}$ chromophore. Both at room temperature and at 90 K the spectrum is axial ($g_{\parallel} = 2.26$, $g_{\perp} = 2.03$). The relation $g_{\parallel} \gg g_{\perp} > 2.0$ indicates a b_1 ($d_{x^2-y^2}$) ground state.[35,36] The spectrum does not show copper hyperfine splitting, which is likely to be the result of a small coupling between the copper(II) ions. The diffuse reflectance spectrum shows a broad ligand-field band with maximum at 8630 cm^{-1}, which agrees with those reported for compounds containing $[CuBr_4]^{2-}$ ions with distorted tetrahedral geometry.[37,38] Two strong Br $\rightarrow$ Cu charge-transfer (CT) transitions involving symmetry-inequivalent π(Br) orbitals are observed at 27 550 and 17 390 cm^{-1} with a shoulder at 15 620 cm^{-1}.[39] The lowering from tetrahedral symmetry splits these bands as evidenced by the low-energy shoulder on the latter.

According to Robin and Day, the mixed-valence compounds can be divided into four classes. The classification is based structurally on the degree of distinguishability of the metal ions.[40] The present compound belongs clearly to class I, where metal ions have very different ligand fields. In this class, the compounds clearly show spectra of constituent ions, as is discussed above. Although there are several mixed-valence Cu(I)/Cu(II) halide species such as a bibridged $[Cu_2Cl_4]_n^-$ chain in $[Et_4N]Cu_2Cl_4$,[41] isolated $[Cu_2Cl_6]^{2-}$ and $[CuCl_2]^-$ anions in $(Bu_4N)_3Cu_3Cl_8$, a tetrameric unit in $[3APy]_4[Cu_4Br_{10}]$[13] (where 3APy = 3-aminopyridinium) and isolated $[CuBr_4]^{2-}$ and $[CuBr_2]^-$ anions in hexakis[bis(ethylenedithio)tetrathiafulvalenium] tetrabromocuprate(II) dibromocuprate(I),[42] the compound $[LH_3]_4[CuBr_4][CuBr_3]\cdot H_2O\cdot 3CH_3OH$ is the first example of a mixed-valence Cu(II)/Cu(I) species containing $[CuBr_4]^{2-}$ and $[CuBr_3]^-$ isolated monomeric anions.

Orientation of the mean planes through co-planar $[LH_3]^+$ ions is approximately similar. Except for one angle and two bond length values in supplementary Table IV, all individual bond lengths and angles of the four organic molecules are the same according to $\pm 2\sigma$ criterion. However, there are some significant differences in the deviation of the atoms from least-squares planes calculated through the molecules (supplementary Table VII). These values indicate minor differences in the configurations of the four molecules.

The LH_2 molecules exist as monovalent cations $[LH_3]^+$ with a neutral carboxylic acid group. In good accord with the IR results, the protonation of $[LH_3]^+$ seems to take place at the nitrogen atom N(8) of the azo group because of the short intramolecular N(8)···O(4) and N(8)···O(16) distances of 2.61 (2)–2.66 (2) and 2.62 (2)–2.67 (2) Å, respectively. Thus the additional proton at N(8) is in a favorable position to participate in an intramolecular bifurcated hydrogen bond between the carbonyl oxygen atom O(4) and oxygen atom O(16) of the carboxylic acid group, the calculated H(8)···O(4) and H(8)···O(16) distances being 1.87–1.91 and 1.89–1.96 Å, respectively. The N(8) atom has also shown to be the protonation site in some compounds containing the analogous $[DZH_2]^+$ ($[DZH_2]^+$ = 6-amino-1,3-dimethyl-5-(phenylazonium)uracil) cation.[2,9,11,43] The same planarity as for $[LH_3]^+$ ions has been also reported for the compounds of $[DZH_2]^+$, in which the proton forms a short intramolecular hydrogen bond between N(8) and O(4). In these both cations, the intramolecular hydrogen bond arrangements seem to contribute to the approximate coplanar configuration of the cations.

Although the estimated standard deviations of the individual bond parameters of $[LH_3]^+$ ions are fairly great, some conclusion can be made. When inspecting the mean bond angle values of $[LH_3]^+$ ions, we observe opening of the C(4)–C(5)–N(7) angle of 125 (3)° away from the O(4) atom, and a corresponding decreasing of the C(6)–C(5)–N(7) angle of 115 (3)°, as compared with the expected value of 120°. Similar angle values have been observed for $[DZEH_2]Br\cdot 2H_2O$ ($[DZEH_2]^+$ = 6-amino-1,3-dimethyl-5-[2′-ethylphenylazonium]uracil) and $[DZH_2][AuCl_2]\cdot 1.5H_2O$ compounds.[8,9] Moreover, some minor changes in the bond angle values around the atoms N(7), N(8), and C(9) can be observed. The C(5)–N(7)–N(8) and N(8)–C(9)–C(10) angles seem to be opened and the N(7)–N(8)–C(9) angle decreased, as compared with the corresponding angles in $[DZEH_2]Br\cdot 2H_2O$ and $[DZH_2][AuCl_2]\cdot 1.5H_2O$. Although all of these small changes are not significant, they seem to balance two different interactions: formation of the bifurcated intramolecular hydrogen bond between

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N(8), O(4), and O(16) and intramolecular repulsion between O(4) and O(16) [O(4)···O(16) = 2.94 (2)-3.04 (2) Å for individual $[LH_3]^+$ ions]. On the other hand, the bond lengths and angles in the pyrimidine and phenyl moieties compare reasonably well with those reported for other complexes of analogous ligands.[2,8,9,11,43]

As stated earlier, the hydrogen atoms could not be found from the difference Fourier map due to the modest quality of the single crystal. Yet, the observed intermolecular contact distances (supplementary Table VIII) suggest a hydrogen-bond network between the cations, anions, and solvent molecules. There are short contact distances between the amino nitrogen of each $[LH_3]^+$ cation and two bromine atoms. Also the geometry supports the assumption that both hydrogen atoms of each amino group participate in hydrogen-bond formation between the atoms (Figure 2). Moreover, three bromine atoms, Br(3), Br(7), and Br(2), seem to form hydrogen bonds with the oxygen atoms of the crystal water molecule, O(503), the methanol molecule, O(501), and the methanol molecule, O(504b), respectively. Thus each bromine atom could participate in one or two hydrogen bonds. The oxygen atoms of the three independent methanol molecules and the crystal water molecule participate in fairly strong hydrogen bonds [O···O = 2.55 (4)-2.65 (3) Å], if only the oxygen-oxygen distances are considered. The assumed hydrogen bonds formed by the solvent molecules probably contribute to the stability of the crystals.

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Registry No. LH_2, 138606-05-0; LH_3Br, 138606-06-1; $[LH_3]_4[CuBr_3][CuBr_4]\cdot H_2O\cdot 3CH_3OH$, 138628-98-5; $(LH_3)_4[CuBr_3][CuBr_4]$, 138629-00-2.

Supplementary Material Available: Tables listing the X-ray diffraction measurement details and complete crystal data (Table SI), atomic coordinates for the four cations, hydrogen atom parameters, and anisotropic thermal parameters for the copper and bromine atoms (Table SII), selected bond lengths and angles for the cations (Table IV), ideal and observed dihedral angles for the $[CuBr_4]^{2-}$ polyhedra (Table V), least-squares mean planes (Table VII), and selected intermolecular contacts (Table VIII) (20 pages); a table of calculated and observed structure factors (26 pages). Ordering information is given on any current masthead page.

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Synthesis, Structure, and Spectral and Magnetic Properties of (μ-Carbonato)(μ-hydroxo)bis[*N*,*N'*-(bis(2-aminoethyl)ethane-1,2-diamine)chromium(III)] Perchlorate

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The μ-carbonato μ-hydroxo complex $[(tren)Cr(\mu\text{-}CO_3)(\mu\text{-}OH)Cr(tren)](ClO_4)_3\cdot 2H_2O$ has been prepared from both Cr(II) and Cr(III) precursors and characterized by structural analysis, magnetic susceptibility measurements, and luminescence spectroscopy. The complex crystallizes in the monoclinic space group $P2_1/c$ (No. 14) with a = 7.022 (1) Å, b = 25.679 (8) Å, c = 8.646 (2) Å, β = 102.27 (2)°, V = 1523.4 (7) Å^3, and Z = 2. Least-squares refinement led to final R and R_w values of 0.054 and 0.043, respectively, for 1857 observed reflections with $F \geq 6\sigma(F)$. In the complex cation, the two Cr(III) centers are in a distorted octahedral environment and are linked by a carbonate and a hydroxide bridge. Within the bridging moiety, Cr-O(CO_3) = 1.954 (4) Å, Cr-O(OH) = 1.944 (2) Å, Cr-OH-Cr = 131.5 (3)°, and O-Cr-O = 94.5 (2)°, while the Cr-N distances are 2.081 (4) Å. Magnetic susceptibility measurements in the temperature range 4.2-300 K indicate that the Cr centers are weakly antiferromagnetically coupled (J = -16.8 cm^{-1}). The luminescence spectrum of the complex at 1.5 K showed four transitions from the luminescent lowest excited state (S^* = 2) to the ground state (S = 0, 1, 2, 3), and from the splitting pattern, a J value of -18.5 (± 0.1) cm^{-1} was determined, consistent with the susceptibility data. The degree of coupling between the metal centers is similar to that observed in related complexes containing hydroxo bridges. A correlation between coupling constant and the average of the shortest Cr-O distance in binuclear Cr(III) complexes similar to that reported for Fe(III) complexes cannot be developed at this stage because of an insufficient number of oxo-bridged complexes with short Cr-O distances.

Introduction

Polynuclear metal complexes are attracting attention not only because of the important functions polynuclear sites perform in biological systems[1] but also because of fundamental interest in understanding the magnetic and spectroscopic properties of these complexes.[2] Numerous complexes are now known in which the metal centers are linked by acetate, oxo, and hydroxo bridging groups,[3] and a clearer picture of the factors affecting M···M interactions is emerging.[2] Correlations between magnetic properties and structural parameters have been developed for Cu(II), Fe(III), and hydroxo-bridged Cr(III) complexes.[2,4] The most recent of these, reported by Gorun and Lippard,[4] suggests that the coupling constants for most doubly and triply bridged Fe(III) complexes follow a relatively simple dependence on the average of shortest metal to bridging group distances.

Comparatively few complexes containing carbonato bridging groups have been structurally characterized, and apart from some Fe(III)[5-7] and Cu(II)[8] complexes, the effect of carbonato bridges

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