of the solutions is rather high, and S_6^{2-} is weakly dissociated. Therefore, the relative increase of S_6^{2-} when the temperature decreases from room temperature to −70 °C is small. Also, the observation of S_6^{2-} by Raman spectroscopy is best done with the 488.0-nm excitation line under resonance conditions, and under these conditions, the species concentration is less easily related to the intensity of the Raman lines.

Discussion

We have previously suggested that the redox dismutation of sulfur in liquid ammonia could be described by the following equation, with the species arbitrarily written as completely ionized:

$$10S + 4NH_3 \rightarrow S_4N^- + S_6^{2-} + 3NH_4^+ \qquad (3)$$

The polysulfide S_6^{2-} is in equilibrium with the radical $S_3^{\bullet -}$:

$$S_6^{2-} \rightleftarrows 2S_3^{\bullet -} \qquad (4)$$

Reaction 3 is oversimplified, first because there must be many kinetic steps to yield such a result and second because S_4N^- is not the only oxidized species detected spectroscopically when solutions have reached equilibrium at room temperature and so other oxidized species may be present. For rather concentrated solutions, S_3N^- has been detected under resonance Raman conditions, at temperatures below 230 K, but the concentration of S_3N^- is certainly very low. If the concentration of S_3N^- were one-tenth of the concentration of S_4N^-, the band of S_3N^- should be clearly observed in the absorption spectrum of about 5×10^{-3} M solutions. It remains that the observation of S_3N^- limits the validity of eq 3. Equation 3 should be correct if the oxidized form of sulfur were only S_4N^-. From eq 3, it appears that the maximum concentration (molarity) of S_4N^- in solution is one-tenth of the sulfur (S) concentration. From Beer's law plotted for the 580-nm absorption band, the extinction coefficient, calculated relative to the sulfur concentration, was found equal to 729 M^{-1} cm^{-1}; this implies that the extinction coefficient of S_4N^- is at least equal to 7290 M^{-1} cm^{-1}. This can be compared to the extinction coefficient of 1.6×10^4 M^{-1} cm^{-1} found for S_4N^- by Chivers et al.[16] The difference cannot be accounted for by the presence of S_3N^-, which has a low concentration.

Other experiments show that the electrochemical impedance in $S-NH_3$ and in $(NH_4)_2S_6-NH_3$ solutions have thermal variations that are governed by eq 4. These experiments show that the S_6^{2-} concentration in $S-NH_3$ solutions is correctly given by eq 3.

It seems therefore that eq 3 describes correctly the redox dismutation of sulfur in liquid ammonia, except that S_4N^- is observed simultaneously with a low concentration of S_3N^-.

It must be emphasized that eq 3 is an overall equation, which does not account for possible transient chemical species during the dissolution process.

Let us say finally that the general type of eq 3 is checked by the fact that progressive addition of base (alkali-metal amide) in the solutions progressively transforms S_4N^- into more oxidized species and S_6^{2-} into more reduced species. Similar equations can easily be written with other oxidized species such as S_3N^-, or other reduced species such as S_4^{2-}, as will be necessary to explain the pH effects.

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Registry No. S, 7704-34-9; NH_3, 7664-41-7; S_4N^-, 74273-17-9; S_6^{2-}, 12597-13-6; $S_3^{\bullet -}$, 12597-04-5; S_3N^-, 76468-83-2.

Contribution from the Department of Chemistry,
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Coordination Compounds of 5-Methyl[1,2,4]triazolo[1,5-*a*]pyrimidin-7-ol. Structures, Spectra, and Unusual Magnetic Properties of Tetraaquabis(5-methyl[1,2,4]triazolo[1,5-*a*]pyrimidin-7-olato)copper(II) and the Structurally Analogous Diammine Diaqua Compound

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The structures of diamminediaquabis(5-methyl[1,2,4]triazolo[1,5-*a*]pyrimidin-7-olato)copper(II), $Cu(C_6H_5N_4O)_2(H_2O)_2(NH_3)_2$ (**1**) and the analogous tetraaqua compound $Cu(C_6H_5N_4O)_2(H_2O)_4$ (**2**) have been determined from X-ray diffraction data. Crystals of both compounds are monoclinic, space group $P2_1/c$, with the following lattice constants: **1**, $a = 8.917$ (2) Å, $b = 13.998$ (2) Å, $c = 7.234$ (5) Å, $\beta = 106.77°$, $Z = 2$; **2**, $a = 9.497$ (3) Å, $b = 13.748$ (2) Å, $c = 6.850$ (4) Å, $\beta = 110.34°$, $Z = 2$. Both compounds appear to have a trans arrangement of the ligands around six-coordinated copper. For **1** $Cu-OH_2(ax)$ is 2.554 (3) Å, $Cu-NH_3$ is 1.997 (3) Å, and Cu–N(lig) is 2.016 (3) Å. For **2** $Cu-OH_2(ax)$ is 2.391 (2) Å, $Cu-OH_2(eq)$ is 2.066 (2) Å, and Cu–N(liq) is 1.962 (2) Å. The structural features of the compounds are related to their spectral and magnetic properties. Though both compounds are essentially mononuclear, magnetic susceptibility measurements show that **1** has a significant magnetic interaction as deduced from the maximum in the susceptibility at 4.1 K. The magnetic exchange coupling in **2**, though it is isostructural, is much smaller. The different properties are explained by different orbital ground states for the two compounds. The magnetic exchange in the "pseudo linear chains" most likely proceeds through ligand-stacking interactions.

Introduction

Purine and pyrimidine derivatives are known to be metal-binding bases in all kinds of biological processes.[1] Therefore, the binding of metal ions to these types of molecules has been studied extensively during recent years. Studies on the naturally occurring bases in DNA have shown that the purine ligands frequently use the imidazole type N(7) atom in coordination, but N(9) may also be used.[2] With adenine there is a bidentate bridge (coordination through N(3) and N(9) has been reported for several copper(II) compounds[3,4]). Pyrimidine bases are also known to use N(3) for coordination to a variety of metal ions.[5] In addition

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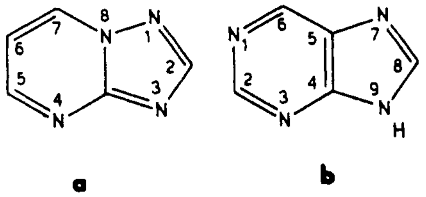

a b

Figure 1. IUPAC numbering for [1,2,4]triazolo[1,5-*a*]pyrimidine (a) and biochemical numbering for purine (b).

to the naturally occurring nucleic acid bases, analogues are used with modified coordination possibilities.[6] These may possess less coordinating atoms or have additional ones. In such cases a different steric or electronic system is usually the result and less reactive donor atoms may be forced to coordinate.

5-Azapurines contain the 1,2,4-triazole nucleus and have no substituents at N(9) or N(7). Therefore, one may expect additional types of coordination. Previously we have studied [1,2,4]triazolo[1,5-*a*]pyrimidines, which resemble the purines, with the main difference being a pyrimidine nitrogen atom in a bridgehead position.[7-9] The numbering of these ring systems has often caused confusion. Therefore, the biological numbering system for purines, used above, is compared in Figure 1 with the IUPAC-recommended numbering for organic compounds. The latter numbering system is used henceforth in this paper.

Our results with 5,7-dimethyl[1,2,4]triazolo[1,5-*a*]pyrimidine (dmtp) have shown that this molecule has a strong preference for N(3) coordination. Although all three non-bridgehead nitrogen atoms are available for coordination, steric reasons probably hamper coordination at N(1) and N(4). On the other hand, the unsubstituted compound (tp) showed more variation[10] in coordination modes: N(1) + N(3), N(3), and N(3) + N(4). Unlike adenine, both guanine and hypoxanthine have a keto oxygen at C(7). This is a possible coordination site, and several authors have suggested N(1) + O(7) chelates with, for instance, platinum compounds for these ligands,[11,12] but evidence from crystal structure determinations is still lacking.

In this study we describe the coordination of metal ions to the compound 5-methyl[1,2,4]triazolo[1,5-*a*]pyrimidin-7-ol (henceforth abbreviated as mtpH). mtpH is an acidic ligand (pK_a = 6.4),[13] with oxygen in the keto form, the C=O stretching absorption occurring at 1700 cm^{-1}. With the deprotonated ligand (mtp) a silver(I) compound has been reported,[14] the structure of which consists of centrosymmetric dimers. Two silver ions are coordinated to the N(3) and N(4) atoms of the two mtp ions. Each silver ion is also weakly bound to the O(7) and N(1) atoms of another dimer, in fact showing one of the rare examples of O(7) coordination. In order to establish whether this type of coordination was also present with other metals, the structures of two copper salts derived from mtpH were investigated. The results, including detailed structural and spectroscopic characterization, are presented in this paper.

Experimental Section

Preparations. Commercially available metal salts were used without further purification. The ligand mtpH was obtained from Janssen Chimica. $\mathrm{Cu(mtp)_2(NH_3)_2(H_2O)_2}$ (**1**) was prepared from a solution of 2 mmol of copper(II) chloride and 4 mmol of mtpH in 40 mL of 10% $\mathrm{NH_4OH}$. The solution was kept at 70 °C. After several hours deep purple crystals had deposited. The product was washed with water and diethyl ether and dried in vacuo at room temperature. $\mathrm{Cu(mtp)_2(H_2O)_4}$ (**2**) was obtained from a solution of copper(II) bromide in 1:1:1 water/ethanol/DMF by a procedure similar to that for **1**. Light green crystals separated when the solution was allowed to stand for several weeks. The compounds prepared by these syntheses gave satisfactory analyses for metal, carbon, hydrogen, and nitrogen.

Table I. Summary of Crystal Data and Collection of Intensities of Compounds **1** and **2**

	1	2
mol formula	$\mathrm{CuC_{12}H_{20}N_{10}O_4}$	$\mathrm{CuC_{12}H_{18}N_8O_6}$
mol wt	431.9	433.8
space group	$P2_1/c$	$P2_1/c$
lattice constants		
a/Å	8.917 (2)	9.497 (3)
b/Å	13.998 (2)	13.748 (2)
c/Å	7.234 (5)	6.850 (4)
β/deg	106.77 (3)	110.34 (3)
Z	2	2
cryst dimens/mm	0.2 × 0.3 × 0.3	0.2 × 0.2 × 0.15
θ range/deg	2–22	2–27.5
range of indices		
h	−8 to +8	−12 to +12
k	−13 to +13	0 to +17
l	−6 to +6	0 to +8
$F(000)$	446	446
no. of indep reflcns	1058	2006
no. of signif reflcns ($I > 2\sigma_I$)	845	1622
final R	3.11	3.60
final R_w	2.63	4.27
d_{obsd}/Mg·m^{-3}	1.65 (2)	1.67 (2)
d_{calcd}/Mg·m^{-3}	1.66	1.67
μ/cm^{-1}	13.10	13.45
range of transmission factors	0.77–0.95	0.78–0.95

Spectroscopic and Magnetic Measurements. Infrared spectra were taken on a Perkin-Elmer Model 580B IR spectrophotometer in the region of 4000–180 cm^{-1}. Samples were measured as KBr or CsCl pellets and as Nujol mulls between polyethene windows (<400 cm^{-1}). Ligand field spectra in the region 28 000–4000 cm^{-1} were recorded on a Perkin-Elmer 330 UV–vis spectrophotometer using the diffuse-reflectance technique with MgO as a reference. ESR spectra were recorded on a Varian E3 (9.5-GHz) spectrometer using powdered samples. Magnetic susceptibility data were obtained on powdered samples in the temperature region 2–80 K on a PAR Model 150A vibrating-sample magnetometer. The observed susceptibilities were fitted to theoretical expressions by means of a least-squares method. $\mathrm{CoHg(SCN)_4}$ was used as a calibrant. The measurements were corrected for diamagnetism (with Pascal constants) and for temperature-independent paramagnetism.

X-ray Data Collection. Single crystals of good quality of **1** and **2** were selected and mounted on an Enraf-Nonius CAD-4 four-circle diffractometer; Mo Kα radiation (λ = 0.71073 Å), monochromated by graphite, was used to determine the unit-cell parameters and the space group, as well as to measure the reflection intensities at room temperature. Diffraction and crystal data are summarized in Table I. The data were corrected for Lorentz and polarization effects and for absorption.[15] The experimental density was determined in a mixture of 1,2-dibromoethane and trichloromethane. Scattering factors were taken from ref 16. All calculations were carried out on the Leiden University computer (Amdahl V7B) using a set of computer programs locally written or modified by E. W. Rutten-Keulemans and R. A. G. de Graaff. The function minimized during least-squares refinement was $\sum w(|F_o| - |F_c|)^2$ with $w = 1/\sigma^2_F$. Reliability indices referred to in Table I are $R = \sum(|F_o| - |F_c|)/|F_o|$ and $R_w = [\sum w(|F_o| - |F_c|)^2/\sum w|F_o|^2]^{1/2}$. The positions of the non-hydrogen atoms were located by using the program AUTOFOUR,[17] written by A.J.K. After several iterations of refinement a difference Fourier yielded the positions of the hydrogen atoms. Further refinement gave the R values stated in Table I. The positional parameters of all atoms and the isotropic B values for the non-hydrogen atoms are listed in Table II. The corresponding labeling of the atoms is given in the

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Table II. Positional Parameters and Isotropic *B* Values ($^8/_3\pi^2$ trace *U*) for Non-Hydrogen Atoms of **1** and **2**[a]

atom	x/a	y/b	z/c	$B_{eq}/Å^2$
		Compound **1**		
Cu*	0.0	0.0	0.0	1.81 (1)
N(A)	0.0554 (4)	−0.0072 (3)	0.2876 (3)	2.45 (8)
O(W)	−0.2823 (3)	0.0418 (2)	−0.0171 (5)	3.24 (7)
N(1)	0.0272 (3)	0.3007 (1)	0.0006 (3)	2.26 (7)
C(2)	−0.0359 (3)	0.2162 (2)	−0.0489 (4)	2.17 (9)
N(3)	0.0555 (2)	0.1400 (1)	0.0218 (3)	1.80 (6)
C(3a)	0.1911 (3)	0.1791 (2)	0.1292 (4)	1.59 (8)
N(4)	0.3190 (3)	0.1344 (1)	0.2310 (3)	1.91 (6)
C(5)	0.4366 (3)	0.1933 (2)	0.3261 (4)	2.05 (8)
C(6)	0.4262 (4)	0.2914 (2)	0.3201 (4)	2.30 (9)
C(7)	0.2925 (3)	0.3404 (2)	0.2109 (4)	2.05 (8)
N(8)	0.1743 (3)	0.2759 (1)	0.1163 (3)	1.73 (6)
C(9)	0.5826 (4)	0.1438 (3)	0.4407 (6)	3.5 (1)
O(10)	0.2678 (2)	0.4273 (1)	0.1902 (3)	2.67 (6)
		Compound **2**		
Cu*	0.0	0.0	0.0	1.816 (9)
O(W1)	0.0812 (2)	0.0256 (1)	0.3171 (3)	2.94 (4)
O(W2)	0.2473 (2)	0.0434 (1)	0.0155 (3)	3.19 (4)
N(1)	0.9778 (2)	0.1992 (1)	0.4795 (2)	2.28 (4)
C(2)	0.0388 (2)	0.2862 (2)	0.5259 (3)	2.34 (4)
N(3)	0.9453 (2)	0.1381 (1)	0.9588 (2)	1.95 (4)
C(3a)	0.8101 (2)	0.1788 (1)	0.8589 (3)	1.72 (4)
N(4)	0.6792 (2)	0.1356 (1)	0.7625 (2)	2.08 (4)
C(5)	0.5631 (2)	0.3034 (1)	0.1761 (3)	2.29 (4)
C(6)	0.5753 (2)	0.2027 (1)	0.1853 (3)	2.38 (4)
C(7)	0.7125 (2)	0.1556 (1)	0.2911 (3)	2.16 (4)
N(8)	0.8297 (2)	0.2225 (1)	0.3730 (2)	1.88 (3)
C(9)	0.4158 (3)	0.3517 (2)	0.0695 (5)	3.65 (6)
O(10)	0.7394 (2)	0.0676 (1)	0.3205 (2)	2.78 (4)

[a] Estimated standard deviations in the last significant digits are given in parentheses. Special positions are marked with an asterisk.

ORTEP[18] drawings in Figure 2. The anisotropic thermal parameters for the non-hydrogen atoms and a list of structure factors are available.[19] By comparison of observed and calculated structure factors it was concluded that no absorption correction was necessary.

Results and Discussion

Description of the Molecular Structure of 1 and 2. The relevant bond distances and bond angles are listed in Table III. The molecular conformations are illustrated in Figure 2. In both compounds the metal ions are six-coordinated and the anionic ligands are coordinated to the copper ion through the N(3) donor atoms. The molecules are mononuclear, and the copper ions are located at an inversion center. In **1** the two N(3) atoms and the two ammonia N atoms constitute a slightly distorted square around copper, Cu–N distances being 2.016 (3) and 1.997 (3) Å, respectively. The two water O atoms in this compound are on axial positions at semicoordinating distances of 2.554 (3) Å. In **2** there are again four relatively short distances around copper, 1.962 (2) Å for Cu–N(3) and 2.066 (2) Å for Cu–O(W1). The other water ligands are bonded perpendicularly to this plane with Cu–O(W2) = 2.391 (2) Å, i.e. much shorter than in **1**. The water molecules in this compound differ from each other in still another way. The hydrogen atoms of O(W1) lie nearly in the CuN_2O_2 equatorial plane, and the angles around oxygen are 110 (3)° for H(W11)–O(W1)–H(W12), 118 (2)° for Cu–O(W1)–H(W11), and 129 (2)° for Cu–O(W1)–H(W12). The geometry around these oxygens can therefore be compared to that of an sp^2 hybridization.[20,21] The angles around the axial oxygen atom however, are much smaller: 82 (3)° for H(W22)–O(W2)–H(W21), 113 (2)° for Cu–O(W2)–H(W22) and 96 (2)° for Cu–O(W2)–H(W21), so that the geometry around these atoms can better be described[20,21] as sp^3. This seems to be in accordance with the difference in the Cu–O distance: short for sp^2 and long for sp^3 hybridization[22] (see Table III). The water molecules in **1** are tetrahedral, which is in accordance with their axial position and with their involvement in the hydrogen-bonding system: O(W)–O(10) = 2.828 (4) Å, O(W)–H(W1)–O(10) = 164 (4)°. The heterocyclic ligands in both compounds are planar; the maximal distance of any ring atom to their least-squares plane

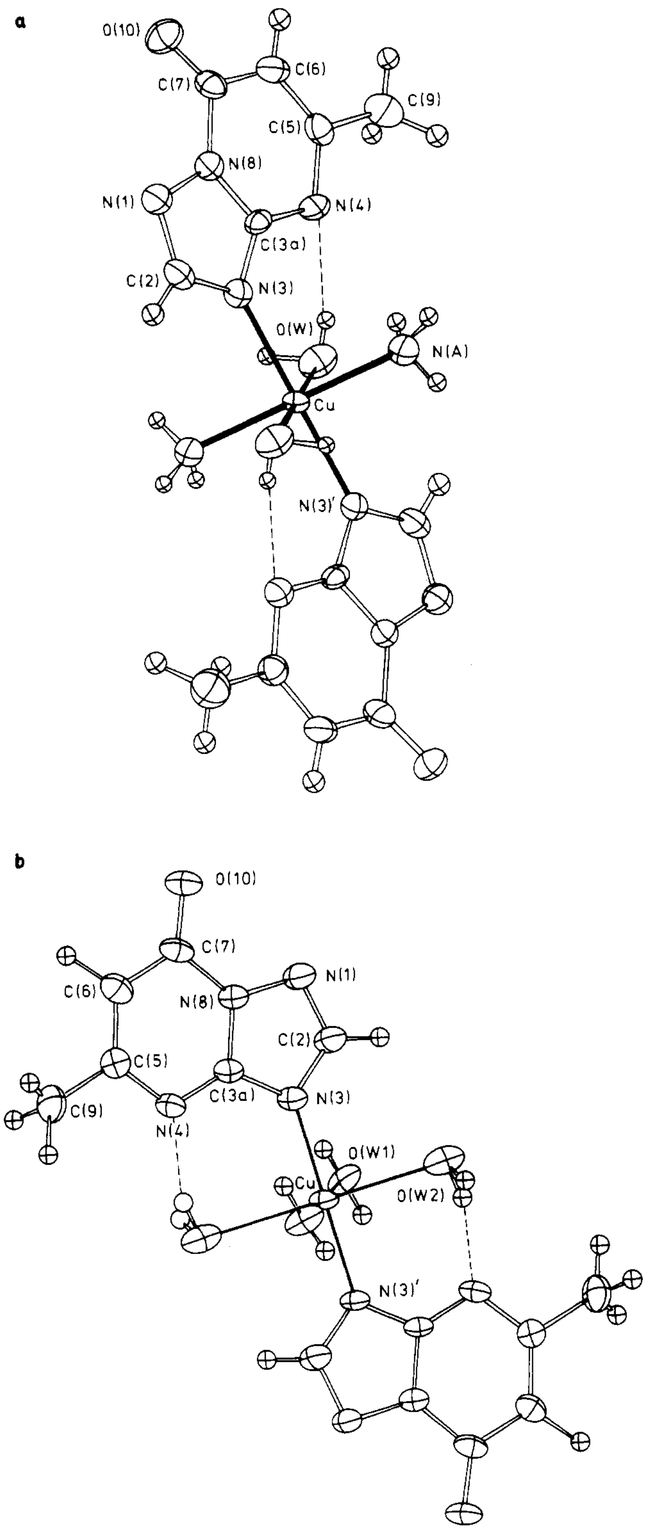

Figure 2. ORTEP[18] drawings for **1** (a) and **2** (b) showing atom labeling. Primed atoms have the symmetry −*x*, −*y*, −*z*.

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Table III. Relevant Bond Distances (Å) and Angles (deg) for Compounds **1** and **2**

	Compound **1**		
Cu–N(A)	1.997 (3)	C(5)–C(6)	1.377 (5)
Cu–N(3)	2.016 (3)	C(6)–C(7)	1.406 (5)
Cu–O(W)	2.554 (3)	C(7)–O(10)	1.237 (4)
C(7)–N(8)	1.406 (4)	N(8)–C(3a)	1.364 (4)
N(8)–N(1)	1.382 (4)	C(5)–C(9)	1.498 (6)
N(1)–C(2)	1.316 (5)	C(2)–H(2)	0.97 (3)
C(2)–N(3)	1.351 (4)	C(6)–H(6)	0.89 (4)
N(3)–C(3a)	1.351 (4)	C(9)–H(91)	0.90 (5)
C(3a)–N(4)	1.323 (4)	C(9)–H(92)	1.00 (5)
N(4)–C(5)	1.356 (5)	C(9)–H(93)	0.82 (5)
O(W)–H(W1)	0.87 (5)	N(A)–H(A2)	0.74 (5)
O(W)–H(W2)	0.72 (4)	N(A)–H(A3)	0.77 (6)
N(A)–H(A1)	0.87 (7)		
N(A)–Cu–N(3)	89.2 (2)	N(A)–Cu–N(3)′	90.8 (2)
N(A)–Cu–O(W)	90.4 (2)	N(A)–Cu–O(W)′	89.6 (2)
O(W)–Cu–N(3)	89.9 (1)	O(W)–Cu–N(3)′	90.1 (1)
N(1)–N(8)–C(7)	125.5 (3)	C(3a)–N(4)–C(5)	114.2 (3)
C(3a)–N(8)–N(1)	110.0 (3)	N(4)–C(5)–C(6)	123.9 (3)
C(3a)–N(8)–C(7)	123.6 (3)	C(5)–C(6)–C(7)	122.8 (3)
N(8)–N(1)–C(2)	101.3 (3)	C(6)–C(7)–C(8)	110.8 (3)
N(1)–C(2)–N(3)	116.3 (4)	N(4)–C(5)–C(9)	114.8 (3)
C(2)–N(3)–C(3a)	104.0 (3)	C(6)–C(5)–C(9)	121.4 (3)
N(8)–C(3a)–N(3)	107.5 (3)	N(8)–C(7)–O(10)	119.4 (3)
N(8)–C(3a)–N(4)	124.7 (3)	C(6)–C(7)–O(10)	129.8 (3)
H(W1)–O(W)–H(W2)	99 (5)	H(A2)–N(A)–H(A3)	108 (6)
H(A1)–N(A)–H(A2)	99 (5)	H(A1)–N(A)–H(A3)	106 (5)
	Compound **2**		
Cu–O(W1)	2.066 (2)	C(5)–C(6)	1.389 (3)
Cu–N(3)	1.962 (2)	C(6)–C(7)	1.411 (3)
Cu–O(W2	2.391 (2)	C(7)–O(10)	1.238 (3)
C(7)–N(8)	1.402 (3)	N(8)–C(3a)	1.371 (3)
N(8)–N(1)	1.378 (2)	C(5)–C(9)	1.491 (3)
N(1)–C(2)	1.320 (3)	C(2)–H(2)	0.89 (2)
C(2)–N(3)	1.341 (3)	C(6)–H(6)	1.17 (2)
N(3)–C(3a)	1.350 (3)	C(9)–H(91)	0.98 (4)
C(3a)–N(4)	1.326 (3)	C(9)–H(92)	0.64 (3)
N(4)–C(5)	1.347 (3)	C(9)–H(93)	1.30 (4)
O(W1)–H(W11)	0.75 (3)	O(W2)–H(W21)	0.83 (4)
O(W1)–H(W12)	1.01 (3)	O(W2)–H(W22)	0.87 (4)
O(W1)–Cu–N(3)	89.19 (7)	O(W1)–Cu–N(3)′	91.81 (7)
O(W1)–Cu–O(W2)	84.75 (8)	O(W1)–Cu–O(W2)′	95.25 (8)
O(W2)–Cu–N(3)	88.42 (7)	O(W2)′–Cu–N(3)	91.58 (1)
N(1)–N(8)–C(7)	125.6 (2)	C(3a)–N(4)–C(5)	114.9 (2)
C(3a)–N(8)–N(1)	111.0 (2)	N(4)–C(5)–C(6)	124.0 (2)
C(3a)–N(8)–C(7)	123.5 (2)	C(5)–C(6)–C(7)	121.9 (2)
N(8)–N(1)–C(2)	101.4 (2)	C(6)–C(7)–C(8)	111.6 (2)
N(1)–C(2)–N(3)	116.1 (2)	N(4)–C(5)–C(9)	114.7 (2)
C(2)–N(3)–C(3a)	104.6 (2)	C(6)–C(5)–C(9)	121.3 (2)
N(8)–C(3a)–N(3)	107.0 (2)	N(8)–C(7)–O(10)	119.1 (2)
N(8)–C(3a)–N(4)	124.1 (2)	C(6)–C(7)–O(10)	129.3 (2)
H(W11)–O(W1)–H(W12)	110 (3)	H(W12)–O(W2)–H(W22)	82 (3)

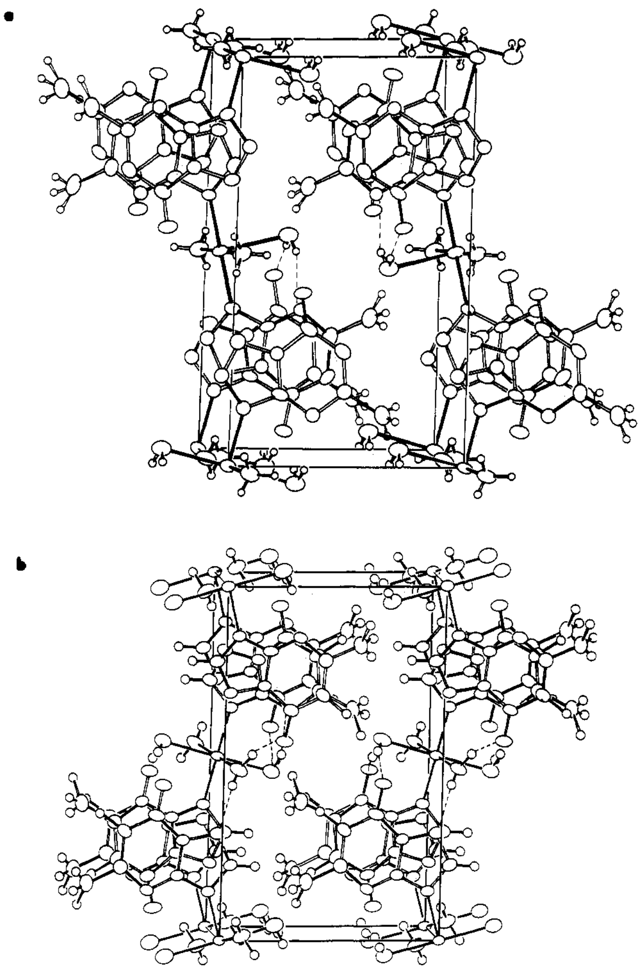

Figure 3. Crystal packing for **1** (a) and **2** (b). Hydrogen bonding is given by dashed lines.

Table IV. Distances (Å) and Angles (deg) Involved in Hydrogen Bridges

compd	H bond X–H–Y	angle	dist X–Y
$Cu(mtp)_2(NH_3)_2$-$(H_2O)_2$ (**1**)	O(W)–H(W2)–N(4)	161 (4)	2.878 (4)
	O(10)–H(W1)–O(W)	164 (4)	2.828 (4)
$Cu(mtp)_2(H_2O)_4$ (**2**)	O(10)–H(W12)–O(W1)	160 (3)	2.789 (2)
	O(W2)–H(W22)–O(10)	159 (3)	2.800 (3)
	O(W1)–H(W11)–N(1)	174 (3)	2.942 (3)
	O(W2)–H(W21)–N(4)	162 (3)	2.847 (3)

Table V. Ligand Field and ESR Parameters of **1** and **2**

compd	LF max/cm^{-1}	ESR spectra *g* values[a]
$Cu(mtp)_2(NH_3)_2(H_2O)_2$ (**1**)	17 700	$g_1 = 2.25$, $g_2 = 2.07$, $g_3 = 2.05$
$Cu(mtp)_2(H_2O)_4$ (**2**)	13 500	$g_1 = 2.30$, $g_2 = 2.14$, $g_3 = 2.04$

[a] At 77 K.

is 0.021 (4) Å in **1** and 0.027 (2) in **2**. Both compounds appear to be packed by stacking of the planar ligands and by hydrogen-bond bridges. The angle between the least-squares planes of the ligand ring atoms is 179.5 (1)° in **1** and 179.8 (1)° in **2**. The distance between the ligand planes is half of the length of the *c* axis, i.e. 3.62 Å in **1** and 3.43 Å in **2**. These distances agree quite well with the van der Waals radius of an aromatic π system.[23] The distance in **2** tends to be somewhat smaller than in comparable compounds, e.g. 3.643 and 3.628 Å in bis(adeninato)(diethylenetriamine)copper(II).[24] The crystal packings are drawn in Figure 3. Table IV gives the hydrogen bridges found for both compounds. There appears to be no involvement of the ammonia hydrogens of **1** in any strong hydrogen bridge. Essentially, both compounds can be regarded as arrays of two-dimensional "plates" of copper ions, i.e. those in the *bc* planes. The copper ions in these plates are connected through stacked ligands and hydrogen bridges. There appear to be only van der Waals forces between the plates. In a comparison of these compounds with the silver compound,[14] it can be observed that there is a great difference in the coordination of the ligand.

Spectral Properties. The infrared spectra of **1** and **2** are quite similar, apart from the water and ammonia vibrations. The free mtpH ligand has a broad maximum at 1700 cm^{-1}, which is ascribed to the C=O stretching vibration. This absorption shifts to 1635 cm^{-1} in **1** and **2**. This shift is likely to be caused by the hydrogen bridging mentioned above. When these compounds are

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(23) *CRC Handbook of Chemistry and Physics*, 60th ed.; CRC: Boca Raton, FL, 1965; p D194.

(24) Sakaguchi, H.; Anzai, H.; Furuhata, K.; Ogura, H.; Iitaka, Y.; Fujita, T.; Sakaguchi, T. *Chem. Pharm. Bull.* **1978**, *26*(8), 2465.

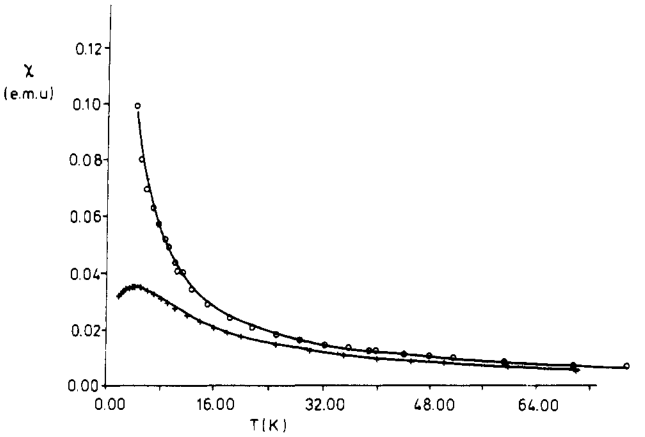

Figure 4. Magnetic susceptibility curves for **1** (+) and **2** (○), together with a theoretical curve corresponding to a Heisenberg chain ($J = -2.54$ cm^{-1} (**1**); $J = -0.25$ cm^{-1} (**2**)).

compared with the silver compound, in which this absorption is observed at 1670 cm^{-1}, it may be concluded that the silver–oxygen coordination has a much smaller effect than the hydrogen bridging in our compounds, in accordance with the semicoordination found (Ag–O = 2.78 Å). The ligand field spectra (Table V) of **1** and **2** both agree with a distorted octahedral coordination. The difference in the positions of the maxima results from the difference in chromophores and the degree of distortion. Table V also lists the ESR *g* values. The rhombic symmetry around the copper ions is reflected by the occurrence of three *g* values. The larger difference for g_2 and g_3 in compound **2** is attributed to the much larger rhombic distortion of **2** compared to that of **1**.

Magnetic Susceptibilities. Figure 4 shows the magnetic susceptibility measurements as a function of the temperature. From the structure analyses it was not quite clear which dimensionality in the magnetic interactions was applicable, because no unambiguous assignment of exchange paths was possible. Preliminary investigations, however, suggested that a one-dimensional copper–copper interaction was sufficient to account for the observed data, which have thus been fitted to such a model[25] (the calculated curves are also drawn in the fugure). The resulting difference in the antiferromagnetic interaction can then be attributed to a difference in electron distribution in the ground state. The two compounds have a different tetragonal distortion, because of which a greater unpaired electron density in the equatorial $d_{x^2-y^2}$ orbital is expected for **1**. In the case of **2** a larger part of the unpaired electron density will be in d_{z^2}, because here we have a weaker (equatorial) ligand field. This d_{z^2} orbital can have no interaction with the ligand π system, because it is in the same plane as the rings, as is seen from inspection of Figures 2 and 3. This implies at the same time that the copper–copper interaction must be transmitted through the stacking of the ligands and not through hydrogen bridges: in **1** there are no hydrogen bridges between the equatorial planes of adjacent copper ions (see Table IV). Further investigations on this matter in connection with the dimensionality of the interaction are in progress.

Concluding Remarks

The present structures show that triazolopyrimidines offer interesting material for mimicking nucleic bases in metal compounds. This study also shows that these types of ligands have stacking possibilities that not only determine the packing in the crystal but may also play an interesting role in the magnetic interactions that metal ions in bioinorganic model compounds can have.

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Supplementary Material Available: Tables SIII and SIV, listing the positional parameters and isotropic temperature factors of the hydrogen atoms, and Tables SV and SVI, listing anisotropic parameters of the non-hydrogen atoms (2 pages); Tables SI and SII, listing calculated and observed structure factors (11 pages). Ordering information is given on any current masthead page.

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Low-Coordinate Lead(II) Complexes with PbP_2C and PbP_4 Coordination. Preparations and Structures of $Pb[(Ph_2P)_2CH]_2$ and $Pb[(Ph_2P)_2C(SiMe_3)]_2$

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The reaction between $PbCl_2$ and $LiCH(PPh_2)_2$ in tetrahydrofuran yields, after cooling and addition of ethyl ether, orange crystals of $Pb[(Ph_2P)_2CH]_2\cdot(CH_3CH_2)_2O$. They crystallize in the monoclinic space group $P2_1/c$ (No. 14) with $a = 18.075$ (8) Å, $b = 14.713$ (6) Å, $c = 18.099$ (8) Å, $\beta = 92.29$ (4)°, $V = 4810$ (4) Å^3, and $Z = 4$ at 130 K. Refinement yielded $R = 0.0571$ for 3899 reflections with $I > 3\sigma(I)$ and 272 parameters. The lead is pyramidal with bonds to two phosphorus atoms of a chelating $(Ph_2P)_2CH^-$ and to one carbon of a monodentate $(Ph_2P)_2CH^-$. A similar reaction between $PbCl_2$ and $Li(Ph_2P)_2C(SiMe_3)$ yields $Pb[(Ph_2P)_2C(SiMe_3)]_2$. This crystallizes from ethyl ether as orange crystals that belong to the orthorhombic space group $P2_12_12_1$ (No. 19) with $a = 17.25$ (4) Å, $b = 11.331$ (12) Å, $c = 26.60$ (4) Å, $V = 5200$ (10) Å^3, and $Z = 4$ at 130 K. Refinement yielded $R = 0.053$ for 2783 reflections with $I > 3\sigma(I)$ and 288 parameters. The structure contains lead bound to the four phosphorus atoms of the two chelating ligands in a distorted-trigonal-bipyramidal geometry with a stereochemically active lone pair. The ^{31}P NMR spectra of both complexes indicate fluxionality. In $Pb[(Ph_2P)_2CH]_2$ the two inequivalent ligands become equivalent in solution at 70 °C, while in $Pb[(Ph_2P)_2C(SiMe_3)]_2$ the two distinct types of phosphorus atoms become equivalent.

Introduction

The structures of lead(II) complexes and the role of the potential lone pair in determining their geometries are poorly defined at present.[1] A wide variation in stoichiometry of lead(II) complexes has been noted.[2] The structures of many species that have been characterized show high coordination numbers, which are frequently achieved through polymerization.[3]

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