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Crystal and Molecular Structure of Tetra-μ-adenine-diaquodicopper(II) Perchlorate Dihydrate, $[Cu_2(C_5H_5N_5)_4(H_2O)_2](ClO_4)_4 \cdot 2H_2O$

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The crystal and molecular structure of the title compound has been determined from three-dimensional X-ray data. The structure was solved by the standard heavy-atom method and refined by least-squares procedures to a conventional R of 0.046 for 2420 observed reflections. The purple complex crystallizes in the monoclinic space group $P2_1/c$ and the cell dimensions are $a = 12.212$ (6), $b = 12.240$ (6), $c = 17.635$ (9) Å, $\beta = 130.27$ (3)°, and $V = 2011.3$ Å^3. The four $Cu(C_5H_5N_5)_2$ units in the cell pair up to form two centrosymmetric dimeric ions, in which adenine acts as a bridging bidentate ligand. Each copper atom is surrounded by four nitrogen atoms (at 2.00–2.04 Å) from four different adenine molecules and by the oxygen atom (at 2.166 Å) of a water molecule. The geometry around copper may be described as a tetragonal pyramid. The four basal nitrogen atoms are coplanar, but the copper atom is displaced from that plane by 0.269 Å toward the apical water molecule. The large Cu–Cu separation (2.951 Å) is not considered to be consistent with significant metal–metal bonding.

Introduction

The importance of metal ions in nucleic acid processes has now been recognized and their involvement in these processes has received considerable attention. They have profound effects on the structure and function of nucleic acids and their constituents. They alter the coding specificity of polynucleotides acting as templates for protein synthesis[1] and are required for stabilizing the structure of tRNA.[2] Model studies with DNA and its constituents have indicated that the ordered structure of the double helix is stabilized by some metal ions (Mg^{2+}, Na^+) and destabilized by other metal ions (Cu^{2+}, Cd^{2+}, Pb^{2+}).

In this paper, we report on the crystal structure of a 1:2 copper perchlorate–adenine (AdH) complex. Our primary interest was the binding sites of the metal to the base in this compound. In $[Cu(AdH_2)_2Br_2]Br_2$,[3] only N9 was found to coordinate to copper, whereas in $[Cu_2(AdH)_4Cl_2]Cl_2 \cdot 6H_2O$,[4] $[Cu_3Cl_8(AdH_2)_2] \cdot 4H_2O$,[5] and $[Cu_2Ad_4(H_2O)_2] \cdot 6H_2O$,[6] adenine acts as a bridging bidentate ligand *via* both N3 and N9. The latter mode of binding is observed for adenine in the present compound.

This work was also expected to provide information on the structural changes induced in the ligand molecule by the metal. This point is particularly relevant to the interpretation of nmr line-broadening experiments. Indeed, the suggestion has been made,[7] and subsequently challenged,[8] that metal ions binding at one site distort the electronic configuration of the whole molecule, so that broadening could occur at sites far removed from the metal. Previous X-ray work on copper–adenine complexes failed to provide meaningful information because of disorder or relatively large uncertainty on the ring bond lengths and angles.

Experimental Section

Crystal Data. A sample of the compound was kindly supplied by Boivin and Zador.[9] The purple crystals are stable to air and to X-rays. The reciprocal lattice symmetry $2/m$ observed from preliminary precession photographs indicated that the crystals are monoclinic. Systematic absences, occuring for $h0l$ reflections when $l = 2n + 1$ and for $0k0$ reflections when $k = 2n + 1$ are consistent only with space group $P2_1/c$. The cell parameters were calculated by least-squares refinement of the setting angles of 12 automatically centered reflections (Cu Kβ radiation, λ 1.39217 Å, $50° < 2\theta < 63°$): $a = 12.212$ (6), $b = 12.240$ (6), $c = 17.635$ (9) Å, $\beta = 130.27$ (3)°, $V = 2011.3$ Å^3, and calculated density of 1.876 g cm^{-3} for $Z = 4$ $C_{10}H_{14}N_{10}Cl_2O_{10}Cu$ units per cell. The density measured by flotation in a mixture of tetrabromoethane and chloroform at 23° is 1.88 ± 0.01 g cm^{-3}. The esd's of the cell parameters are assigned twice the values computed in the least-squares refinement, which reflects our experience with reproducibility of results.

There was a small but significant difference between the cell parameters obtained at the beginning and at the end of data collection. The average values reported above were used to calculate the bond distances and bond angles. The same calculations were done as well with the two extreme sets of cell parameters. This changed the Cu–Cu distance by 1σ, but the other bond lengths and angles were affected by less than 0.5σ.

Collection and Reduction of Intensity Data. The intensity data were collected from a well-formed crystal of dimensions $0.14 \times 0.18 \times 0.11 \times 0.09$ mm (perpendicular to the $\{100\}$, $\{011\}$, $\{11\bar{1}\}$, and $\{\bar{1}11\}$ faces, respectively). The crystal was mounted on a Picker FACS-1 four-circle automatic diffractometer with its c axis along the ϕ axis of the instrument. Ni-filtered Cu Kα radiation was used and the takeoff angle was 4°. The source-to-crystal distance was 16 cm and the crystal-to-counter distance was 35 cm. The data were collected with the θ–2θ scan technique, at a scan rate of $1°(2\theta)$/min. The scan range was 1.7° applied symmetrically to the calculated 2θ value. A dispersion factor of $114.6\Delta\lambda/\lambda$, where $\Delta\lambda$ is the difference between $\lambda(K\alpha_1)$ and $\lambda(K\alpha_2)$ and λ is $\lambda(K\bar{\alpha})$, was added to the high side of 2θ to allow for the separation of the $\alpha_1\,\alpha_2$ doublet. Stationary-counter, stationary-crystal background counts of 40 sec were taken at each limit of the scan range. During the course of the data collection, three standard reflections were measured at a period of 30 reflections. Their variations were less than 2% from their respective means.

A total of 4061 measurements were made in the region of $2\theta < 120°$ and reduced to a set of 2957 independent reflections, after averaging the equivalent ones and taking out 170 systematically absent reflections. The integrated intensity was calculated as $I(\text{net}) = I(\text{scan}) - K(B_1 + B_2)$, where I(scan) is the count over the scan range, B_1 and B_2 are the background counts, and K is the ratio of the

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[1] W. Szer and S. Ochoa, *J. Mol. Biol.*, 8, 823 (1964).

[2] J. R. Fresco, A. Adams, R. Ascione, D. Henley, and T. Lindahl, *Cold Spring Harbor Symp. Quant. Biol.*, 31, 527 (1966).

[3] P. De Meester, D. M. L. Goodgame, K. A. Price, and A. C. Skapski, *Biochem. Biophys. Res. Commun.*, 44, 510 (1971).

[4] P. De Meester and A. C. Skapski, *J. Chem. Soc. A*, 2167 (1971).

[5] P. De Meester, D. M. L. Goodgame, K. A. Price, and A. C. Skapski, *Chem. Commun.*, 1573 (1970).

[6] E. Sletten, *Acta Crystallogr., Sect. B*, 25, 1480 (1969).

[7] J. A. Carrabine and M. Sundaralingam, *J. Amer. Chem. Soc.*, 92, 369 (1970).

[8] N. A. Berger and G. L. Eichhorn, *Biochemistry*, 10, 1847 (1971).

[9] The crystals were isolated from a water solution containing adenine (0.015 *M*) and $Cu(ClO_4)_2$ (0.005 *M*) at pH 4.0. They are undoubtedly identical with those prepared by R. Weiss and H. Venner, *Z. Physiol. Chem.*, 341, 229 (1965), and formulated as $[(C_5H_5N_5)_2Cu](ClO_4)_2 \cdot 1.5H_2O$.

Table II. Final Structure Parameters[a] and Estimated Standard Deviations[b]

Atom	x	y	z	$10^4\beta_{11}$	$10^4\beta_{22}$	$10^4\beta_{33}$	$10^4\beta_{12}$	$10^4\beta_{13}$	$10^4\beta_{23}$
Cu	0.04989 (6)	0.11405 (5)	0.02854 (4)	60.1 (6)	38.1 (4)	20.7 (3)	0.4 (4)	22.6 (4)	0.4 (3)
Cl1	0.48869 (15)	0.37621 (14)	0.19790 (9)	143 (2)	118 (1)	43.5 (8)	−68 (1)	49 (1)	−26 (1)
Cl2	0.85132 (12)	0.0028 (1)	0.22057 (9)	93 (1)	84 (1)	42.4 (7)	0.6 (9)	40 (1)	2.7 (7)
O1	0.3827 (4)	0.3488 (5)	0.2049 (3)	136 (6)	173 (6)	85 (3)	−61 (5)	67 (4)	−7 (4)
O2	0.5198 (8)	0.4863 (5)	0.2123 (5)	526 (17)	141 (6)	190 (7)	−190 (8)	270 (10)	−109 (5)
O3	0.4449 (6)	0.3428 (4)	0.1045 (3)	324 (9)	89 (4)	44 (2)	−53 (5)	79 (4)	−14 (2)
O4	0.6166 (5)	0.3181 (7)	0.2738 (4)	152 (7)	333 (11)	64 (3)	14 (7)	54 (4)	20 (5)
O5	0.9211 (5)	0.0895 (3)	0.2128 (4)	202 (7)	88 (4)	115 (4)	−23 (4)	115 (5)	−15 (3)
O6	0.9414 (6)	−0.0375 (5)	0.3177 (3)	291 (10)	198 (7)	58 (3)	77 (7)	87 (5)	51 (4)
O7	0.7255 (5)	0.0491 (6)	0.1943 (5)	117 (6)	258 (8)	149 (5)	22 (6)	97 (5)	3 (6)
O8	0.8188 (6)	−0.0811 (4)	0.1541 (4)	316 (10)	90 (4)	83 (4)	−42 (5)	101 (5)	−28 (3)
O9	0.1024 (3)	0.2861 (3)	0.0450 (2)	107 (4)	46 (2)	51 (2)	−18 (3)	40 (3)	−9 (2)
O10	−0.1390 (8)	0.4221 (6)	−0.0746 (5)	422 (14)	169 (7)	129 (5)	125 (8)	181 (8)	78 (5)
N1	−0.2913 (4)	0.2465 (3)	0.0104 (3)	102 (5)	49 (3)	48 (2)	−5 (3)	52 (3)	−9 (2)
C2	−0.1696 (5)	0.2279 (4)	0.0276 (3)	97 (6)	47 (3)	43 (3)	−3 (3)	47 (4)	−6 (2)
N3	−0.1322 (3)	0.1355 (3)	0.0093 (2)	73 (4)	44 (3)	27 (2)	8 (3)	32 (3)	−1 (2)
C4	−0.2298 (4)	0.0546 (4)	−0.0273 (3)	57 (5)	49 (3)	25 (2)	6 (3)	25 (3)	5 (2)
C5	−0.3612 (5)	0.0676 (4)	−0.0506 (3)	88 (6)	47 (3)	31 (2)	7 (3)	35 (3)	3 (2)
C6	−0.3951 (5)	0.1676 (4)	−0.0335 (3)	103 (6)	64 (4)	34 (3)	12 (4)	43 (4)	6 (3)
N7	−0.4291 (4)	−0.0311 (3)	−0.0856 (3)	68 (4)	59 (3)	40 (2)	−12 (3)	31 (3)	−8 (2)
C8	−0.3387 (5)	−0.0984 (4)	−0.0819 (3)	80 (5)	54 (4)	44 (3)	−5 (4)	40 (4)	−7 (3)
N9	−0.2173 (3)	−0.0494 (3)	−0.0470 (2)	63 (4)	46 (3)	31 (2)	0 (3)	29 (3)	−4 (2)
N10	−0.5205 (4)	0.1895 (3)	−0.0549 (3)	105 (5)	70 (3)	67 (3)	22 (3)	64 (4)	2 (3)
N1*	0.2870 (4)	0.1072 (3)	0.3431 (2)	103 (5)	52 (3)	24 (2)	−11 (3)	29 (3)	−1 (2)
C2*	0.2255 (5)	0.1355 (4)	0.2504 (3)	103 (6)	43 (3)	37 (3)	−9 (3)	39 (4)	−1 (2)
N3*	0.1481 (4)	0.0715 (3)	0.1691 (2)	70 (4)	48 (2)	23 (2)	−2 (3)	24 (3)	−2 (2)
C4*	0.1361 (4)	−0.0324 (3)	0.1886 (3)	61 (5)	38 (3)	24 (2)	3 (3)	25 (3)	2 (2)
C5*	0.1960 (4)	−0.0683 (3)	0.2821 (3)	63 (5)	41 (3)	29 (2)	−4 (3)	29 (3)	0 (2)
C6*	0.2728 (4)	0.0045 (4)	0.3622 (3)	70 (5)	53 (3)	27 (2)	−2 (3)	27 (3)	4 (2)
N7*	0.1573 (4)	−0.1771 (3)	0.2697 (2)	96 (5)	47 (3)	23 (2)	−1 (3)	29 (3)	6 (2)
C8*	0.0794 (5)	−0.2009 (4)	0.1729 (3)	95 (6)	46 (3)	36 (3)	−9 (3)	37 (3)	−5 (2)
N9*	0.0639 (3)	−0.1152 (3)	0.1207 (2)	68 (4)	42 (2)	24 (2)	2 (3)	26 (2)	5 (2)
N10*	0.3309 (4)	−0.0224 (3)	0.4550 (3)	126 (5)	54 (3)	25 (2)	−14 (3)	36 (3)	0 (2)

Hydrogens	x	y	z	B, Å^2	Hydrogens	x	y	z	B, Å^2
HC2	−0.101 (4)	0.295 (3)	0.055 (3)	1.7 (8)	HC2*	0.235 (5)	0.215 (4)	0.241 (3)	3.3 (10)
HN7	−0.512 (5)	−0.045 (4)	−0.112 (3)	3.5 (10)	HN7*	0.187 (5)	−0.225 (4)	0.315 (3)	3.3 (10)
HC8	−0.363 (5)	−0.176 (4)	−0.106 (4)	3.9 (11)	HC8*	0.039 (4)	−0.275 (3)	0.147 (3)	2.4 (9)
H1N10	−0.532 (5)	0.260 (4)	−0.048 (4)	4.5 (12)	H1N10*	0.363 (5)	0.031 (4)	0.496 (3)	3.0 (10)
H2N10	−0.583 (5)	0.133 (4)	−0.087 (4)	4.8 (13)	H2N10*	0.322 (4)	−0.091 (3)	0.467 (3)	1.8 (8)
H1O9	0.178 (5)	0.316 (4)	0.078 (3)	3.2 (10)	H1O10	−0.165 (9)	0.461 (8)	−0.124 (6)	11 (2)
H2O9	0.052 (5)	0.323 (4)	0.019 (4)	4.0 (11)					

[a] The anisotropic thermal parameters are in the form $\exp(-h^2\beta_{11} - k^2\beta_{22} - l^2\beta_{33} - 2hk\beta_{12} - 2hl\beta_{13} - 2kl\beta_{23})$. [b] Standard deviations are given in parentheses. Identifiers with an asterisk refer to adenine molecule 2.

total scan time to the total background time. A reflection was considered as observed when I(net) = >8 and $>0.1K(B_1 + B_2)$. By these criteria, 2420 reflections were retained. An absorption correction based on the equations of the crystal faces was applied to each reflection. The transmission factors calculated with the linear absorption coefficient of 47.0 cm^{-1} for Cu Kα radiation ranged from 0.58 to 0.70. Finally, the Lorentz and polarization corrections were applied.

Solution and Refinement of the Structure. The structure was solved by the standard heavy-atom method and refined by full-matrix least squares initially and by block-diagonal least squares in the later stages. The copper position was evident from the three-dimensional Patterson map. A Fourier synthesis phased on this position revealed the positions of 14 additional atoms. These positions were refined and the next Fourier synthesis revealed all nonhydrogen atoms. Refinement proceeded normally using the block-diagonal least-squares approximation and converged initially at an R_1 $(=\Sigma||F_o| - |F_c||/\Sigma|F_o|)$ of 0.105, after varying the positional and individual isotropic temperature factors for all nonhydrogen atoms. Inclusion of anisotropic temperature factors reduced R_1 to 0.053. At this stage, a secondary extinction correction was entered. A difference map showed ten peaks of 0.5–0.7 e/Å^3, suggesting positions for the hydrogens of the adenine ligands. Inclusion of these positions in the refinement reduced R_1 to 0.047. A series of three difference maps with data limited to $(\sin\theta)/\lambda$ = <0.5, <0.4, and <0.3 revealed three peaks whose heights remained about the same in all three maps (~0.45 e/Å^3). These peaks, although not higher than the background by more than 0.05 e/Å^3, were taken as the positions for three of the four hydrogens of the water molecules and entered in the refinement. The last hydrogen was not located. At this point, a weighting scheme was introduced: $\sqrt{w} = |F_o|/17.0$ for $|F_o| < 17.0$ and $\sqrt{w} = 17.0/|F_o|$ for $|F_o| > 17.0$. Three further cycles of refinement were performed in which the positional parameters of all atoms, the anisotropic temperature factors of nonhydrogen atoms, and the isotropic temperature factors of hydrogen atoms were varied. The final R_1 was 0.046 (observed data) and $R_2 = (\Sigma w(|F_o| - |F_c|)^2/\Sigma w|F_o|^2)^{1/2}$ was 0.056 (observed and unobserved data). The function $w(|F_o| - |F_c|)^2/N$, where N is the number of reflections in the particular range, showed no significant variation with $|F_o|$ or h (the slowest varying index during data collection) but showed a small decreasing trend with $(\sin\theta)/\lambda$. Average and maximum shifts in the final least-squares refinement were 0.1σ and 0.3σ, respectively. The scattering factors for all atoms were taken from Cromer and Waber[10] and the anomalous dispersion components for Cu and Cl were taken from Cromer.[11]

The calculated and observed structure factors are listed in Table I[12] and the refined atomic parameters are found in Table II.[13]

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(10) D. T. Cromer and J. T. Waber, *Acta Crystallogr., Sect. B*, **18**, 104 (1965).

(11) D. T. Cromer, *Acta Crystallogr., Sect. B*, **18**, 17 (1965).

(12) Table I, a listing of observed and calculated structure factors will appear following these pages in the microfilm edition of this volume of the journal. Single copies may be obtained from the Business Operations Office, Books and Journals Division, American Chemical Society, 1155 Sixteenth St., N.W., Washington, D. C. 20036. Remit check or money order for $3.00 for photocopy or $2.00 for microfiche, referring to code number INORG-73-1166.

(13) The computer programs used were locally modified versions of the following: F. R. Ahmed and C. P. Huber, NRC-2 (data reduction); F. R. Ahmed and P. Singh, NRC-3 (absorption correction); C. T. Prewitt, SFLS5 (least-squares refinement); A. Zalkin, FORDAP (Fourier and Patterson maps); R. J. Doedens and J. A. Ibers, NUCLS (least-squares refinement), with block diagonal option introduced by J. Sygusch; C. K. Johnson, ORTEP (drawings).

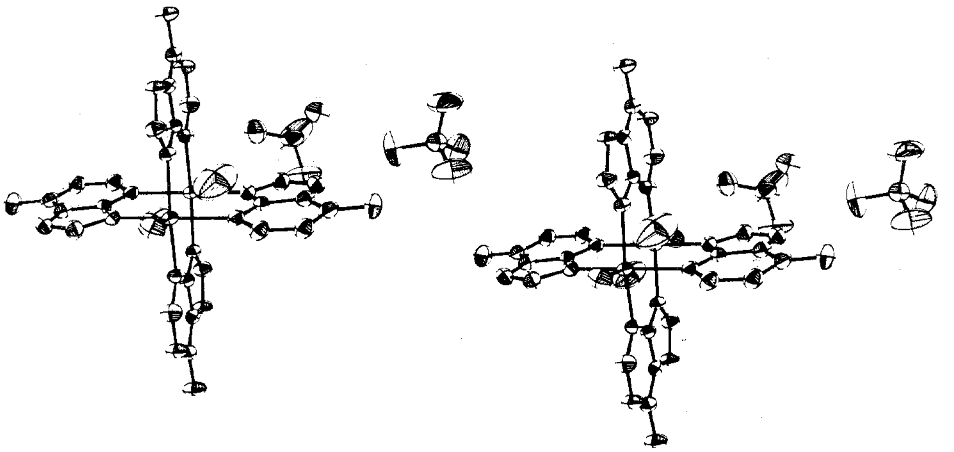

Figure 1. The molecular structure of the $[Cu_2(AdH)_4(H_2O)_2]^{4+}$ ion. The ellipsoids correspond to 50% probability. The hydrogen atoms are not included.

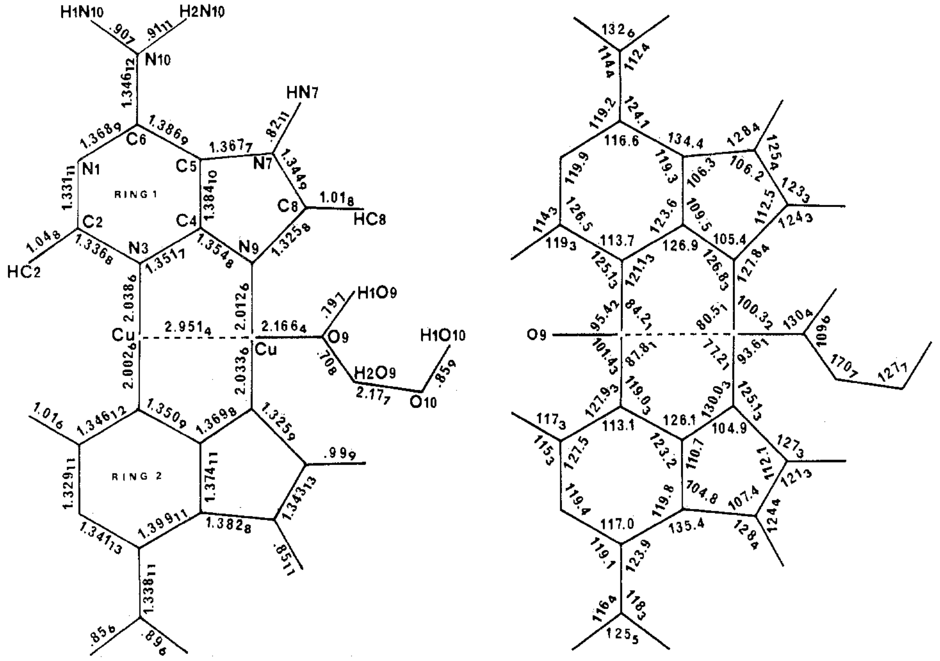

Figure 2. Bond distances and angles in the $[Cu_2(AdH)_4(H_2O)_2]^{4+}$ ion. Standard deviations are given as subscripts. When not indicated, the standard deviations on the angles are 0.5°.

Results and Discussion

Environment of Copper. The structure contains the centrosymmetric $[Cu_2(AdH)_4(H_2O)_2]^{4+}$ cation, in which adenine acts as a bridging bidentate ligand *via* N3 and N9 (Figure 1). The bond lengths and angles in the complex ion are given in Figure 2.

Each copper atom is surrounded by four nitrogen atoms (at 2.00-2.04 Å) from four different adenine molecules and by the oxygen atom (at 2.166 (4) Å) of a water molecule. The other copper atom in the dimer is found at 2.951 (4) Å. This complex ion may be considered as the N7 tetraprotonated form of the inner complex $[Cu_2Ad_4(H_2O)_2]$ previously studied.[6] It is also similar to $[Cu_2(AdH)_4Cl_2]^{2+}$,[4] the apical position being occupied by a water molecule instead of a chlorine atom. The four nitrogen atoms coordinated to a given copper atom are coplanar within 0.005 Å (1σ), but the metal is displaced from that plane by 0.269 (2) Å toward the apical water molecule. Displacements in the range 0.27-0.33 Å have been observed for similar complexes.[4,6,14]

The Cu-Cu separation appears to be primarily determined by the width of the "bite" of the bridging ligand (~3.05 Å[6]), but there seems to be some dependence on the apical ligand. In $[Cu_2(AdH)_4Cl_2]^{2+}$ [4] and the corresponding hypoxanthine complex,[14] the apical ligand is a chlorine atom and the Cu-Cu distances are 3.006 (4) and 3.024 (4) Å, respectively. In $[Cu_2Ad_4(H_2O)_2]$[6] and in the present $[Cu_2(AdH)_4(H_2O)_2]^{4+}$ ion, the apical position is occupied by a water molecule and significantly shorter distances of 2.949 (2) and 2.951 (4) Å, respectively, have been observed. All those distances are relatively large and the copper atoms are not generally considered to be bonded. On the basis of the very small value calculated for the overlap integral of an hypothetical Cu-Cu δ bond of 2.64 Å in $[Cu_2(acetate)_4(H_2O)_2]$,[15] Sletten[6] concluded that the δ bonding should be vanishingly small when the copper atoms are 2.95 Å apart. This conclusion is consistent with the X-band epr spectrum,[16] which is reported to be characteristic of a species with a spin of 1. Similarly, no significant metal-metal bond is as-

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(14) E. Sletten, *Acta Crystallogr., Sect. B*, 26, 1609 (1970).

(15) L. Dubicki and R. L. Martin, *Inorg. Chem.*, 5, 2203 (1966).

(16) R. W. Duerst, S. J. Baum, and G. F. Kokoszka, *Nature (London)*, 222, 665 (1969).

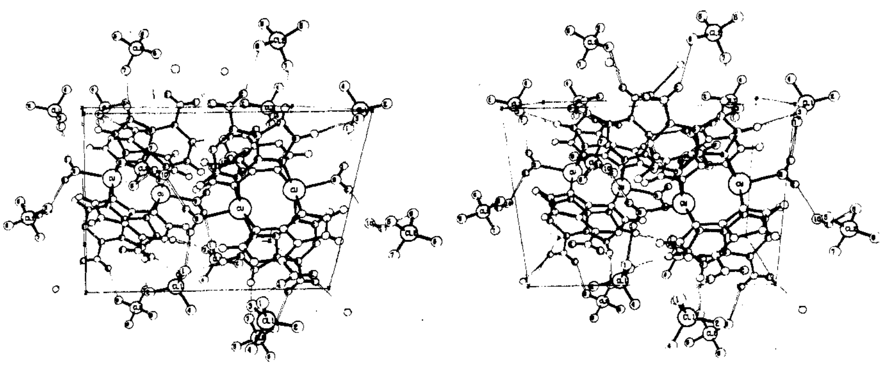

Figure 3. Stereoscopic illustration of the packing of $[Cu_2(AdH)_4(H_2O)_2](ClO_4)_4 \cdot 2H_2O$. Hydrogen bonds are indicated by light lines. The viewer is looking down the *a* axis, with the *b* axis parallel to the interocular line. Only the numerical part of the labels are given and the labels for ligand 2 have been omitted for clarity. The atoms can be identified by comparison with Figure 2.

sumed to exist in $[Cu_2(AdH)_4Cl_2]^{2+}$ and the subnormal value of 1.45 BM for the magnetic moment is interpreted in terms of a superexchange mechanism involving the bridging adenine molecules.[4] The above arguments apply to the present complex as well and the X-band epr spectrum also favors the absence of appreciable Cu-Cu bonding.[16] Consequently, the copper environment should be described as a tetragonal pyramid in this compound.

For the coordinated adenine molecule 1, the Cu-N3 bond (2.038 (6) Å) is a little longer than the Cu-N9 bond (2.012 (6) Å), whereas the reverse is observed for adenine molecule 2 (Cu-N3* = 2.002 (6) Å, Cu-N9* = 2.033 (6) Å). This inversion is probably due to packing forces and to the different hydrogen-bonding schemes of the two adenine ligands (see below). In the three copper-adenine (or -hypoxanthine) dimers studied previously,[4,6,14] the Cu-N9 bonds were always found to be slightly shorter than the Cu-N3 bonds and this was interpreted as an evidence for a larger s character in the coordinating orbital of the imidazole N9 atom. The ligands were disordered in two of these structures,[6,14] while for the third one,[4] the difference between Cu-N3 and Cu-N9 is within 3σ. Our results do not warrant this generalization.

Geometry of the Adenine Ligands. The bond lengths and angles of the two crystallographically independent adenine ligands are given in Figure 2. It is difficult to make meaningful comparisons with the other similar structures, because of their disorder or relatively high standard deviations.[4,6,14] Instead, we have compared with the adenine moiety in several nucleotides.

The structural changes produced by protonation of N1 have been discussed by Rao and Sundaralingam.[17] They noticed that N1 protonation increases the angle C6-N1-C2 from 118-120 to ~123.5° but decreases C5-C6-N1 from 117-118 to ~113.5°. The values observed for C6-N1-C2 (119.4, 119.9°) and C5-C6-N1 (116.6, 117.0°) confirm that N1 is not protonated in this complex.

The binding of copper to N3 has some effect on the ligand geometry near N3. Differences are found for C2-N3-C4 (113.1, 113.7°) and N3-C4-C5 (123.2, 123.6°), which do not fall within the corresponding ranges observed for the nucleotides (110-112 and 126-128°, respectively).

The geometries of the imidazole moieties also exhibit significant differences. Protonation of N7 has an effect on C4-C5-N7 (104.8, 106.3°) and C8-N7-C5 (106.2, 107.4°), these angles being generally 110.5-111.6 and 103-105°, respectively, in the neutral bases.[17] The imidazole ring of guanine is also protonated at N7 in $(C_5H_6N_5O)CuCl_3 \cdot H_2O$[7] and it shows similar values for the above angles. The C5-C4-N9 angles in the guanine complex (110.9°) and in the present compound (109.5, 110.7°) are 4-5° greater than usually found,[17] which may reflect the influence of the copper atom at N9.

Table III. Bond Distances and Bond Angles in the Perchlorate Ions

Atoms	Dist, Å	Atoms	Dist, Å
Cl1-O1	1.417 (8)	Cl2-O5	1.422 (6)
Cl1-O2	1.378 (9)	Cl2-O6	1.397 (7)
Cl1-O3	1.424 (9)	Cl2-O7	1.406 (9)
Cl1-O4	1.426 (12)	Cl2-O8	1.409 (9)
Atoms	Angle, deg	Atoms	Angle, deg
O1-Cl1-O2	111.8 (4)	O5-Cl2-O6	109.5 (4)
O1-Cl1-O3	110.6 (4)	O5-Cl2-O7	105.6 (5)
O1-Cl1-O4	107.9 (4)	O5-Cl2-O8	109.2 (4)
O2-Cl1-O3	110.2 (4)	O6-Cl2-O7	111.9 (5)
O2-Cl1-O4	108.0 (5)	O6-Cl2-O8	109.8 (4)
O3-Cl1-O4	108.1 (4)	O7-Cl2-O8	110.9 (4)

Table IV. Hydrogen Bond Lengths and Angles

Atoms	Angle, deg	Length, Å	Length from hydrogen, Å
N7-HN7· · ·O7	167 (5)	2.802 (12)	2.00 (8)
N10-H1N10· · ·N1*	133 (5)	3.080 (10)	2.39 (6)
N10-H2N10· · ·O8	141 (5)	3.139 (14)	2.38 (8)
N7*-HN7*· · ·N1	145 (5)	3.224 (9)	2.49 (8)
N10*-H1N10*· · ·O3	176 (5)	2.995 (8)	2.15 (8)
N10*-H2N10*· · ·N1	180 (5)	2.999 (9)	2.11 (7)
O9-H1O9· · ·O1	156 (5)	2.789 (10)	2.04 (8)
O9-H2O9· · ·O10	170 (7)	2.806 (14)	2.17 (9)
O10-H1O10· · ·O6	137 (9)	2.99 (2)	2.32 (11)

In the nucleotides, the N7-C8 and C8-N9 bond lengths are generally 1.30-1.315 and 1.36-1.39 Å, respectively,[17] which indicates a higher bond order for N7-C8. Comparable bond lengths were observed for the copper-guanine complex,[7] but in the present complex, C8-N9 (1.325 Å) was found to be shorter than N7-C8 (1.345 Å) for both adenine molecules. This presumably indicates a redistribution of the π-electron density over N7-C8-N9 to increase the double-bond character of C8-N9 compared to N7-C8. The reason that this effect is not observed for the guanine complex is not obvious.

Several least-squares planes were calculated as a check for the planarity of the purine rings in the ligands. For ring 2, no atom is more than 0.01 Å (1σ) from the mean plane through the nine atoms of the ring, while for ring 1, distances as large as 0.05 Å have been calculated. The greater distortion of ring 1 is also revealed by the dihedral angle of

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[17] S. T. Rao and M. Sundaralingam, *J. Amer. Chem. Soc.*, **92**, 4963 (1970).

2.9° between the mean plane through the six atoms of the pyrimidine ring and the mean plane through the five atoms of the imidazole moiety, respectively. This angle is less than 0.4° for ring 2. For both adenine molecules, the nitrogen atoms of the amino groups are pulled out of the planes of the purine rings by ~0.06 (1) Å. The copper atom is found at 0.072 (2) Å from that same plane for ring 2, but a much greater distance of 0.209 (2) Å is observed for ring 1. All these deviations are most likely due to the different hydrogen-bonding schemes in which the two independent ligands are involved.

Packing and Hydrogen Bonding. Figure 3 shows how the $[Cu_2(AdH)_4(H_2O)_2]^{4+}$ cations, the ClO_4^- anions, and the lattice water molecules are held together in an intricate network of hydrogen bonds.

From Figure 1, it is obvious that the oxygen atoms in the perchlorate groups have a large thermal motion (isotropic B ranging from 6 to 11 Å^2). However, all the bond lengths and angles (Table III) are quite reasonable and there is no evidence for disorder in these anions from the difference Fourier map.

Table IV lists a series of intermolecular contacts involving hydrogen, most of which undoubtedly correspond to hydrogen bonds. The hydrogen atom H2O10 of one of the water molecules was not located, but a search around O10 revealed no basic site close enough to imply appreciable hydrogen bonding through the missing hydrogen. The table shows that the atoms N7 and N1 of ring 1 are involved in rather strong hydrogen bonding and it is reasonable to believe that this can result in significant distortions in the ring. On the other hand, ring 2 forms strong hydrogen bonds only through the hydrogen atoms of the amino group. This group being removed from the ring itself, little distortion is expected in the ring, in agreement with the above observations.

Registry No. $[Cu_2(C_5H_5N_5)_4(H_2O)_2](ClO_4)_4 \cdot 2H_2O$, 38744-29-5.

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Crystal Structure of *cyclo*-Tri-μ-(trimethylphosphine sulfide)-tris(chlorocopper(I))

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The crystal structure of the copper(I) complex $[Cu((CH_3)_3PS)Cl]_3$ has been determined from three-dimensional X-ray data collected by counter methods. The material crystallized in space group C_s^3-Im of the monoclinic system, with two trimeric units in a cell of dimensions $a = 6.294$ (3), $b = 20.399$ (12), $c = 9.271$ (5) Å, and $\beta = 99.04$ (2)° (temperature 25°). The observed and calculated densities are 1.75 and 1.755 g cm^{-3}, respectively. The structure was solved by conventional heavy-atom methods and has been refined to a final R factor of 0.024 on F, using 2501 independent reflections having $F_o^2 \geqslant 3\sigma(F_o^2)$. The molecular structure consists of a six-membered ring of alternating Cu atoms and bridging S atoms which is bisected by a crystallographic mirror plane. The ring is puckered into a chair conformation with equatorial $(CH_3)_3P$ groups, and the phosphine sulfide is symmetrically bridged. The copper atoms are three-coordinate, with approximately trigonal-planar coordination to two bridging S atoms of the phosphine sulfides and one terminal chlorine atom. The bond angles about the S and P atoms are nearly tetrahedral. Important bond distances follow: Cu–S, 2.265 (1) Å; Cu–Cl, 2.209 (2) and 2.220 (1) Å; S–P, 2.025 (1) Å.

Introduction

While investigating the coordination properties of phosphine sulfide ligands with copper(I), we found that the preferred coordination number is apparently 3 rather than 2 or 4.[2] In fact, the X-ray structure determination of $[Cu((CH_3)_3PS)_3]ClO_4$ showed that the cation contained a trigonal-planar arrangement of sulfur atoms around the copper atom.[3]

Another class of compounds, $[CuLX]_n$ (X = Cl, Br, I, SCN; L = tertiary phosphine sulfide), has recently been isolated.[4] On the basis of their relative insolubilities, we assumed that these compounds were polymeric. For the complexes $[Cu((CH_3)_3PS)X]_n$ (X = Cl, Br, I) the shift of the P–S stretching frequency upon coordination of $(CH_3)_3PS$ (as observed from their infrared spectra) was twice as large as the shift for $[Cu((CH_3)_3PS)_3]ClO_4$ (40–45 and 25 cm^{-1}, respectively). The larger shift of the P–S infrared absorption in the halide complexes was attributed to sulfur atom bridges,[4] even though few bridging phosphine sulfides have ever been proposed.[5]

The X-ray structural determination of $[Cu((CH_3)_3PS)Cl]_3$, which is reported herein, was undertaken to clarify (1) the nature of the polymer, (2) the bridging atom, and (3) the coordination number and geometry of copper(I) in this compound. To our knowledge this is the first X-ray determination of the structure of a complex involving a bridging phosphine sulfide ligand. A preliminary account of the structure has been reported.[6]

Experimental Section

Microcrystalline $[Cu((CH_3)_3PS)Cl]_3$ was readily prepared by

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[1] (a) Ohio State University Postdoctoral Fellow, Sept 1971–Sept 1972. (b) Postdoctoral Research Associate.

[2] J. A. Tiethof, A. T. Hetey, P. E. Nicpon, and D. W. Meek, *Inorg. Nucl. Chem. Lett.*, 8, 841 (1972).

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[6] J. A. Tiethof, J. K. Stalick, P. W. R. Corfield, and D. W. Meek, *J. Chem. Soc., Chem. Commun.*, 1141 (1972).