

Correction d'absorption: non  
 3914 réflexions mesurées  
 3914 réflexions indépendantes  
 1867 réflexions observées  
 $[I > 3\sigma(I)]$   
 $\theta_{\max} = 29^\circ$

$l = 0 \rightarrow 22$   
 3 réflexions de référence  
 (10 $\bar{1}$ , 00 $\bar{2}$ , 0 $\bar{1}$ 1)  
 mesurées tout les 60 réflexions  
 variation d'intensité: < 1%

(1971); programme *MACORTEP* (Michalowicz & Andre, 1991) utilisé pour le dessin de la structure.

Les listes des facteurs de structure, des facteurs d'agitation thermique anisotrope, des coordonnées des atomes d'hydrogène et des liaisons de van der Waals (< 3,60 Å) ont été déposées au dépôt d'archives de la British Library Document Supply Centre (Supplementary Publication No. SUP 55944: 27 pp.). On peut en obtenir des copies en s'adressant à: The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, Angleterre. [Référence de CIF: DU1013]

### Affinement

Affinement basé sur les  $F$   
 $R = 0,035$   
 $wR = 0,031$   
 $S = 1,5$   
 1867 réflexions  
 101 paramètres  
 $w = 1/\sigma^2(F)$

$(\Delta/\sigma)_{\max} = 0,6$   
 $\Delta\rho_{\max} = 0,33 \text{ e } \text{Å}^{-3}$   
 $\Delta\rho_{\min} = -0,28 \text{ e } \text{Å}^{-3}$   
 Facteurs de diffusion de  
*International Tables for*  
*X-ray Crystallography*  
 (1974, Tome IV)

Tableau 1. Coordonnées atomiques et facteurs d'agitation thermique isotropes équivalents (Å<sup>2</sup>)

$$U_{\text{eq}} = (1/3)[\text{trace (U) orthogonalisé}].$$

	x	y	z	$U_{\text{eq}}$
Rh	0,44429 (4)	0,13778 (4)	0,46885 (2)	0,0204 (1)
O(1)	0,5218 (4)	0,0654 (4)	0,3318 (2)	0,026 (2)
O(2)	0,6684 (3)	0,2534 (4)	0,5027 (2)	0,025 (2)
O(3)	0,2269 (3)	0,0071 (4)	0,4392 (2)	0,025 (2)
O(4)	0,3744 (4)	0,1956 (4)	0,6092 (2)	0,026 (2)
O(51)	0,3301 (4)	0,4018 (4)	0,4121 (2)	0,034 (2)
C(1)	0,5936 (5)	-0,0838 (6)	0,3219 (3)	0,025 (2)
C(2)	0,6440 (7)	-0,1335 (7)	0,2191 (3)	0,043 (3)
C(3)	0,7846 (5)	0,1572 (6)	0,5400 (3)	0,025 (2)
C(4)	0,9505 (5)	0,2455 (7)	0,5604 (4)	0,036 (3)
C(52)	0,3499 (7)	0,4546 (7)	0,3119 (4)	0,046 (3)

Tableau 2. Paramètres géométriques (Å, °)

Environnement du Rh	Ligands acétate	
Rh—Rh <sup>i</sup>	2,3777 (6)	O(1)—C(1)
Rh—O(1)	2,039 (3)	C(1)—C(2)
Rh—O(2)	2,038 (3)	C(1)—O(4) <sup>i</sup>
Rh—O(3)	2,032 (3)	O(2)—C(3)
Rh—O(4)	2,032 (3)	C(3)—C(4)
Rh—O(51)	2,288 (3)	C(3)—O(3) <sup>i</sup>
	Ligand méthanol	
	O(51)—C(52)	1,415 (6)
Environnement du Rh	Ligands acétate	
Rh <sup>i</sup> —Rh—O(1)	87,59 (8)	O(1)—C(1)—C(2)
O(1)—Rh—O(51)	93,8 (1)	C(4)—C(3)—O(3) <sup>i</sup>
Rh <sup>i</sup> —Rh—O(2)	88,30 (8)	O(1)—C(1)—O(4) <sup>i</sup>
O(2)—Rh—O(3)	176,2 (1)	Rh—O(1)—C(1)
Rh <sup>i</sup> —Rh—O(3)	87,90 (8)	C(2)—C(1)—O(4) <sup>i</sup>
O(2)—Rh—O(4)	89,4 (1)	Rh—O(2)—C(3)
Rh <sup>i</sup> —Rh—O(4)	88,72 (8)	O(2)—C(3)—C(4)
O(2)—Rh—O(51)	92,9 (1)	Rh—O(3)—C(3) <sup>i</sup>
Rh <sup>i</sup> —Rh—O(51)	178,16 (9)	O(2)—C(3)—O(3) <sup>i</sup>
O(3)—Rh—O(4)	90,3 (1)	Rh—O(4)—C(1) <sup>i</sup>
O(1)—Rh—O(2)	90,1 (1)	
O(3)—Rh—O(51)	90,9 (1)	Ligand méthanol
O(1)—Rh—O(3)	89,9 (1)	Rh—O(51)—C(52)
O(4)—Rh—O(51)	89,9 (1)	
O(1)—Rh—O(4)	176,3 (1)	

Code de symétrie: (i) 1 - x, -y, 1 - z.

Correction des facteurs de Lorentz-polarisation; localisation de l'atome lourd par la méthode de Patterson puis affinement des positions atomiques et des facteurs de températures par la méthode des moindres carrés avec le programme de Busing

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### Structure of Dibromobis(2-chloroimidazole)copper(II)

GIOVANNI VALLE

*Centro di Studio sui Biopolimeri del CNR, Dipartimento di Chimica Organica, Università di Padova, Padova, Italy*

ANGELES SÁNCHEZ GONZÁLEZ

*Departamento de Química Inorganica, Universidad de Santiago de Compostela, Santiago de Compostela, Spain*

RENATO ETTORRE\*

*Dipartimento di Chimica Inorganica, Metallorganica e Analitica, Università di Padova, Padova, Italy*

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### Abstract

The structure of [CuBr<sub>2</sub>(C<sub>3</sub>H<sub>3</sub>ClN<sub>2</sub>)<sub>2</sub>] consists of discrete four-coordinate molecular units with two imidazole N(3) atoms and two bromide ions bonded to the metal. The coordination about the Cu atom is

intermediate between tetrahedral and square-planar. The complex is isostructural with the corresponding chloride  $[\text{CuCl}_2(\text{C}_3\text{H}_3\text{ClN}_2)_2]$ .

### Comment

This report on the complex  $[\text{CuBr}_2(\text{C}_3\text{H}_3\text{ClN}_2)_2]$  (I) is related to previous work on the corresponding chloride  $[\text{CuCl}_2(\text{C}_3\text{H}_3\text{ClN}_2)_2]$  (II) (Valle, Sánchez González & Eitorre, 1991). The intermolecular  $\text{Cu}\cdots\text{Br}$  distances are greater than 4.0 Å. Close intermolecular contacts at the Br atoms are  $\text{N}(1)\cdots\text{Br}(1)$  ( $\frac{3}{2} - x, \frac{1}{2} - y, 1 - z$ ) of 3.476 (8) Å and  $\text{Br}(1)\cdots\text{Cl}(2)$  ( $\frac{1}{2} - x, -\frac{1}{2} + y, \frac{1}{2} - z$ ) of 3.442 (2) Å. The complexes (I) and (II) are isostructural. Both the configuration at the Cu atom and the conformation about the Cu—N bonds for (I) and (II) are practically identical. Coordination bond angles in (II) are  $\text{N}(3)\text{—Cu—N}(3')$  151.1 (1),  $\text{Cl}(1)\text{—Cu—Cl}(1')$  141.8 (1),  $\text{Cl}(1)\text{—Cu—N}(3)$  94.9 (1) and  $\text{Cl—Cu—N}(3')$  94.5 (1)°. Torsion angles measured were  $\text{Br}(1)\text{—Cu—N}(3)\text{—C}(2)$   $-80.9$  (6)° for (I) and  $\text{Cl}(1)\text{—Cu—N}(3)\text{—C}(2)$   $-80.2$  (3)° for (II). The dihedral angles between the planes through the two imidazole ligands are 53.3 (3)° for (I) and 52.7 (2)° for (II). Unlike the two 2-chloroimidazole complexes, (I) and (II), there is a difference between the *N*-methylimidazole complexes  $[\text{CuBr}_2(\text{C}_4\text{H}_6\text{N}_2)_2]$  (III) (Jansen, van Koningsveld & van Ooijen, 1978) and  $[\text{CuCl}_2(\text{C}_4\text{H}_6\text{N}_2)_2]$  (IV) (van Ooijen, Reedijk & Spek, 1979). The coordination is distorted octahedral for the bromide (III) but close to that in (I) and (II) for the chloride (IV).

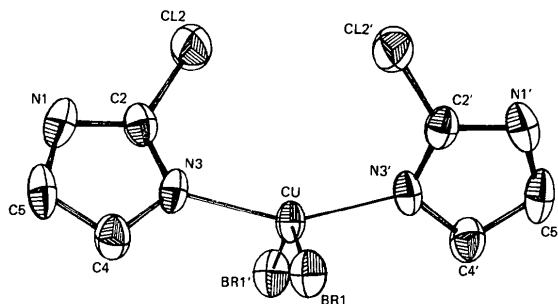


Fig. 1. Molecular scheme with the atomic numbering and thermal ellipsoids drawn at the 50% probability level.

### Experimental

#### Crystal data

$[\text{CuBr}_2(\text{C}_3\text{H}_3\text{ClN}_2)_2]$

$M_r = 428.4$

Monoclinic

$C2/c$

$a = 8.277$  (1) Å

$b = 12.720$  (2) Å

$c = 11.887$  (2) Å

$\beta = 91.0$  (1)°

Mo  $K\alpha$  radiation

$\lambda = 0.7107$  Å

Cell parameters from 25 reflections

$\theta = 7\text{--}13^\circ$

$\mu = 8.48$   $\text{mm}^{-1}$

Room temperature

Irregular

$V = 1251.3$  (3) Å<sup>3</sup>

$Z = 4$

$D_x = 2.27$   $\text{Mg m}^{-3}$

$0.3 \times 0.2 \times 0.1$  mm

Green

Crystal source: chemical synthesis

#### Data collection

Philips PW1100 diffractometer

$\theta$ - $2\theta$  scans

Absorption correction: none

3002 measured reflections

1508 independent reflections

1197 observed reflections  
[ $F > 7\sigma(F)$ ]

$R_{\text{int}} = 0.13$

$\theta_{\text{max}} = 56.0^\circ$

$h = -10 \rightarrow 9$

$k = -15 \rightarrow 15$

$l = 0 \rightarrow 10$

3 standard reflections

monitored every 180

reflections

intensity variation: 10%

#### Refinement

Refinement on  $F$

Final  $R = 0.074$

$wR = 0.076$

$S = 0.83$

1197 reflections

69 parameters

H-atom parameters not refined

$w = 1/[\sigma^2(F) + 0.0136F^2]$

$(\Delta/\sigma)_{\text{max}} = 0.192$

$\Delta\rho_{\text{max}} = 2.8$   $\text{e Å}^{-3}$

(near Br)

$\Delta\rho_{\text{min}} = -3.0$   $\text{e Å}^{-3}$

(near Br)

Atomic scattering factors from *SHELX76* and *International Tables for X-ray Crystallography* (1974, Vol. IV)

Table 1. Fractional atomic coordinates and equivalent isotropic thermal parameters (Å<sup>2</sup>)

$$U_{\text{eq}} = \frac{1}{3} \sum_i \sum_j U_{ij} a_i^* a_j^* a_i a_j$$

	<i>x</i>	<i>y</i>	<i>z</i>	$U_{\text{eq}}$
Cu	1.0000	0.14056 (8)	0.2500	0.0337 (4)
Br(1)	0.73018 (7)	0.07469 (6)	0.27475 (6)	0.0429 (3)
Cl(2)	0.8832 (3)	0.3629 (2)	0.3887 (2)	0.0609 (8)
N(1)	1.0220 (9)	0.2651 (6)	0.5693 (6)	0.054 (2)
N(3)	1.0342 (7)	0.1784 (5)	0.4108 (4)	0.038 (2)
C(2)	0.9814 (8)	0.2636 (6)	0.4576 (6)	0.041 (2)
C(4)	1.1092 (9)	0.1191 (6)	0.4947 (6)	0.046 (2)
C(5)	1.101 (1)	0.1762 (8)	0.5931 (6)	0.056 (3)

Table 2. Bond lengths (Å) and angles (°)

Cu—Br(1)	2.408 (1)	Cu—N(3)	1.987 (5)
N(3)—Cu—N(3)'	152.0 (3)	Br(1)—Cu—N(3)	94.8 (2)
Br(1)—Cu—N(3)'	94.9 (2)	Br(1)—Cu—Br(1)'	139.3 (1)

The Cu atom was first located from a Patterson map using *SHELXS86* (Sheldrick, 1986). A difference Fourier map then revealed the other atoms (*SHELX76*; Sheldrick, 1976). The quite large  $R$  and  $R_{\text{int}}$  values are due to the quality of the crystal and its decay.

Lists of structure factors, anisotropic thermal parameters, H-atom coordinates and hydrogen-bond geometry have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 55903 (11 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England. [CIF reference: NA1027]

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**Hexaaquadisodium Hexakis(tetramethylammonium) Bis[bis(3-acetyl-amino-4-hydroxyphenylarsonato)aquaoctadeca-oxohexamolybdate] Decahydrate:**  
 $[\text{Na}_2(\text{H}_2\text{O})_6][(\text{CH}_3)_4\text{N}]_6[\text{Mo}_6(\text{C}_8\text{H}_8\text{AsNO}_5)_2\text{O}_{18}(\text{H}_2\text{O})_2]_2 \cdot 10\text{H}_2\text{O}$

XIAO-ZENG YOU AND HAI-LIAN LI

Coordination Chemistry Institute, Nanjing University,  
Nanjing, 210008, People's Republic of China

KAI-BEI YU AND LIU LI

Chendu Analysis Center of the Academy of Sciences of  
China, 610041, People's Republic of China

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**Abstract**

Di- $\mu$ -aqua-tetraaquadisodium hexakis(tetramethylammonium) bis[ $\mu_4$ -(3-acetyl-amino-4-hydroxyphenylarsonato)-1:2 $\kappa^2\text{O}$ ,3 $\kappa\text{O}'$ ,6 $\kappa\text{O}'$ ]- $\mu_6$ -(3-acetyl-amino-4-hydroxyphenylarsonato)-1:6 $\kappa^2\text{O}$ ,2:3 $\kappa^2\text{O}'$ ,4:5 $\kappa^2\text{O}'$ ]- $\mu$ -aqua-4:5 $\kappa^2\text{O}$ -hexa- $\mu$ -oxo-1:2 $\kappa^2\text{O}$ ;1:6 $\kappa^2\text{O}$ ;2:3 $\kappa^2\text{O}$ ;3:4 $\kappa^2\text{O}$ ;4:5 $\kappa^2\text{O}$ ;-5:6 $\kappa^2\text{O}$ -dodecaoxo-1 $\kappa^2\text{O},\text{O}'$ ;2 $\kappa^2\text{O},\text{O}'$ ;3 $\kappa^2\text{O},\text{O}'$ ;4 $\kappa^2\text{O},\text{O}'$ ;-5 $\kappa^2\text{O},\text{O}'$ ;6 $\kappa^2\text{O},\text{O}'$ ]-hexamolybdate decahydrate {dimer of  $[\text{Na}(\text{H}_2\text{O})_3][(\text{CH}_3)_4\text{N}][\text{Mo}_6(\text{C}_8\text{H}_8\text{AsNO}_5)_2\text{O}_{18}(\text{H}_2\text{O})]$ } has been crystallized. The unit cell contains two  $[\text{Mo}_6(\text{C}_8\text{H}_8\text{AsNO}_5)_2\text{O}_{18}(\text{H}_2\text{O})]^{4-}$  complex anions linked by two  $\text{Na}^+$  cations associated with six water molecules, six  $[(\text{CH}_3)_4\text{N}]^+$  cations and another ten water molecules of hydration.

**Comment**

Polyoxomolybdates are oxo transfer catalysts, potential photosensitizers and electron relay species in the redox cycle. The synthesis, solution properties, and structure of a series of polymolybdate anions based on monoalkyl- and monoarylarsonates ( $\text{RASO}_3$ ) $^{2-}$  have been studied

previously by Adams, Klemperer & Liu (1979), Zonneville & Pope (1979), and You, Chen, Xu & Huang (1989).

The molecular structure consists of  $[(\text{CH}_3)_4\text{N}]^+$  cations,  $[\text{Mo}_6(\text{C}_8\text{H}_8\text{AsNO}_5)_2\text{O}_{18}(\text{H}_2\text{O})]^{4-}$  anions and  $\text{Na}^+$  cations coordinated by water molecules and the carbonyls of the acetyl groups. The molybdate anions are linked by the  $[\text{Na}_2(\text{H}_2\text{O})_6]^{2+}$  cation via the carbonyl O atoms O(29) and O(29') to form an  $\{[\text{Na}_2(\text{H}_2\text{O})_6][\text{Mo}_6(\text{C}_8\text{H}_8\text{AsNO}_5)_2\text{O}_{18}(\text{H}_2\text{O})]_2\}^{6-}$  dimer lying on a centre of symmetry (Figs. 1 and 2).

The anion may be viewed as six distorted octahedra joined together by shared edges to form an approximately flat metal oxide ring, which is capped, top and bottom, by 3-acetyl-amino-4-hydroxyphenylarsonate ligands. The water molecule  $\text{H}_2\text{O}(18)$  bridges the Mo atoms Mo(4) and Mo(5) in place of the arsonate O atoms O(14) and O(25), which only singly coordinate to Mo atoms Mo(3) and Mo(6), respectively [ $\text{O}(14) \cdots \text{Mo}(4) = 4.342$ ,  $\text{O}(25) \cdots \text{Mo}(5) = 3.845 \text{ \AA}$ ]. This results in the loss of the

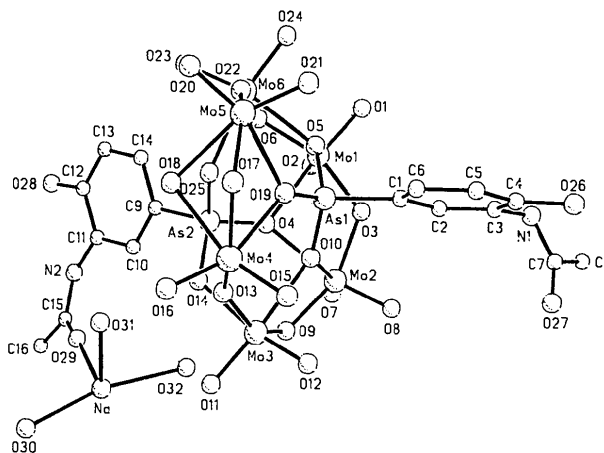


Fig. 1. Structure of the  $[\text{Mo}_6(\text{C}_8\text{H}_8\text{AsNO}_5)_2\text{O}_{18}(\text{H}_2\text{O})]^{4-}$  anion.

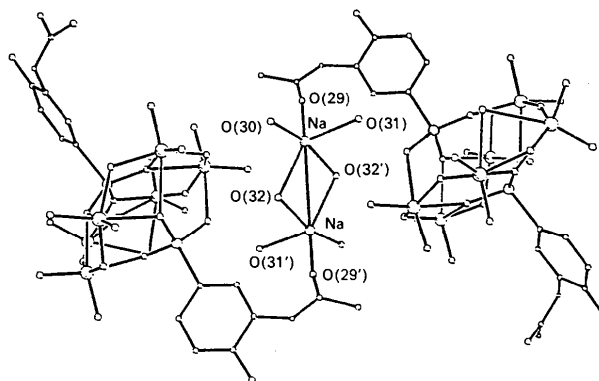


Fig. 2. View of the  $\{[\text{Na}_2(\text{H}_2\text{O})_6][\text{Mo}_6(\text{C}_8\text{H}_8\text{AsNO}_5)_2\text{O}_{18}(\text{H}_2\text{O})]_2\}^{6-}$  dimer.