acetone/dichloromethane mixture and exposed to air. After 1 d, 8.2 mg (75%) of 1,1′-bis(diphenylphosphine oxide)ferrocene were obtained as red–brown crystals.

Crystal data

$[Fe(C_{17}H_{14}OP)_2].H_2O$
$M_r = 604.37$
Monoclinic
$P2_1/c$
$a = 22.5535\,(1)$ Å
$b = 10.4998\,(1)$ Å
$c = 12.1717\,(2)$ Å
$\beta = 96.116\,(1)^\circ$
$V = 2865.94\,(6)$ Å^3
$Z = 4$
$D_x = 1.401$ Mg m^{-3}
D_m not measured

Mo $K\alpha$ radiation
$\lambda = 0.71073$ Å
Cell parameters from 8192 reflections
$\theta = 1–25^\circ$
$\mu = 0.672$ mm^{-1}
$T = 173$ K
Cylinder
$0.40 \times 0.15 \times 0.10$ mm
Red–brown

Data collection

Siemens CCD three-circle diffractometer
ω scans
Absorption correction: empirical (*SADABS*; Sheldrick, 1996*a*)
$T_{min} = 0.778$, $T_{max} = 0.935$
28 822 measured reflections
5287 independent reflections

3907 reflections with $I > 2\sigma(I)$
$R_{int} = 0.075$
$\theta_{max} = 26.32^\circ$
$h = -27 \rightarrow 27$
$k = -12 \rightarrow 13$
$l = -14 \rightarrow 13$
254 standard reflections
frequency: 480 min
intensity decay: none

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.074$
$wR(F^2) = 0.142$
$S = 1.123$
5287 reflections
366 parameters
H atoms: see below
$w = 1/[\sigma^2(F_o^2) + (0.0324P)^2 + 7.705P]$ where $P = (F_o^2 + 2F_c^2)/3$

$(\Delta/\sigma)_{max} = 0.005$
$\Delta\rho_{max} = 0.498$ e Å^{-3}
$\Delta\rho_{min} = -0.536$ e Å^{-3}
Extinction correction: none
Scattering factors from *International Tables for Crystallography* (Vol. C)

The data collection nominally covered over a sphere of reciprocal space, by a combination of seven sets of exposures; each set had a different φ angle for the crystal and each exposure covered 0.3° in ω. The crystal-to-detector distance was 6.0 cm. Coverage of the unique set was over 99% complete to at least 26° in θ. Crystal decay was monitored by repeating the initial frames at the end of data collection and analyzing the duplicate reflections. The H atoms attached to the ordered C atoms and the hydroxyl H atoms could be located by difference Fourier synthesis; the disordered atoms being positioned with ideal geometry. While the two hydroxyl H atoms were refined isotropically, the others were refined with fixed individual displacement parameters [$U(H) = 1.2U_{eq}(C)$] using a riding model with C—H = 0.95 Å. The ratio of the site occupation factors of the disorded atoms (C62, C63, C65 and C66) refined to 0.53 (1).

Data collection: *SMART* (Siemens, 1995). Cell refinement: *SMART*. Data reduction: *SAINT* (Siemens, 1995). Program(s) used to solve structure: *SHELXS*86 (Sheldrick, 1990). Program(s) used to refine structure: *SHELXL*96 (Sheldrick, 1996*b*). Molecular graphics: *XP* (Sheldrick, 1991).

Supplementary data for this paper are available from the IUCr electronic archives (Reference: AV1015). Services for accessing these data are described at the back of the journal.

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Redetermination of Bis(2-aminopyrimidinium) Tetrabromocopper(II) at 200 and 100 K

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Abstract

The structure of $(C_4H_6N_3)_2[CuBr_4]$ has been studied using X-ray diffraction techniques at 200 and 100 K. The molecular structure has ideal square-planar $[CuBr_4]^{2-}$ groups, bonded to protonated organic mol-

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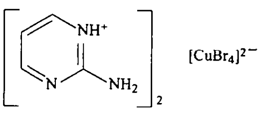
ecules not only through hydrogen bonds, but also *via* the lone pair of one N atom through a coordinative Cu—N bond, so making the other N atom protonated. The copper coordination changes slightly at lower temperatures towards an octahedral coordination. The compound presents Jahn–Teller distortion as confirmed by magnetic measurements; there is antiferromagnetic ordering at T_n = 30 K, with a broad peak indicating that the system is one-dimensional.

Comment

Square-planar $[CuBr_4]^{2-}$ ions are extremely rare, even more so than $[CuCl_4]^{2-}$ (Antolini, Benedetti, Fabretti & Giusti, 1988). Most of the $[CuBr_4]^{2-}$ anions reported previously (Patyal, Scott & Willett, 1990; Scott & Willet, 1991) have distorted tetrahedral geometries. It is necessary to find the appropriate organic molecules which can be protonated in acidic medium to give cations suitable for the formation of stable hydrogen bonds with $[CuBr_4]^{2-}$ ions.

In the present compound, however, we have found that the $[CuBr_4]^{2-}$ ions have ideal square-planar Cu coordination. In fact, the angles between the Cu—Br bonds are 90.02 (5) and 90.08 (3)° for the structures at 200 K, (I), and 100 K, (II), respectively. This is because of the interaction between the Cu atom and two N atoms from the two 2-aminopyrimidine molecules. From this, we can explain the molecular geometry in terms of the Jahn–Teller effect.



$(C_4H_6N_3)_2[CuBr_4]$

The room temperature crystal structure of this compound has been reported recently (Pon, Willet, Prince, Robinson & Turnbull, 1997). We performed a variable temperature study of this compound and report the complementary structural results at 200 and 100 K (Cosier & Glazer, 1986).

The copper coordination changes slightly at lower temperatures towards an octahedral coordination. The N—Cu distances change from 2.787 (6) at room temperature to 2.734 (4) at 100 K. The Cu—Br distances and angles are very similar in this temperature range. The structures show Br···Br distances between molecules varying from 4.088 (2) (room temperature) to 4.007 (2) at 100 K. Otherwise, the interatomic distance between the two Br atoms coordinating to the same Cu atom are shorter than the sum of their van der Waals radii: 3.476 (1) Å at 200 K and 3.464 (1) Å at 100 K.

In the high-temperature range (150–350 K) of the magnetic susceptibility, the compound has a localized paramagnetic moment of 1.37 μB, in agreement with the presence of a Cu^{2+} ion ($3d^9$). This, however, is different from the theoretical value and could be assigned to the presence of the Jahn–Teller distortion.

Other similar compounds have displayed reversible thermochromism with variations in temperature (Fernández, Morán, Gutiérrez-Ríos, Foces-Foces & Cano, 1987), but in this case, a possible colour change could not be observed due to the very dark colour of the crystals. Nevertheless, the structural results show the gradual change of the N—Cu distance towards an octahedral coordination.

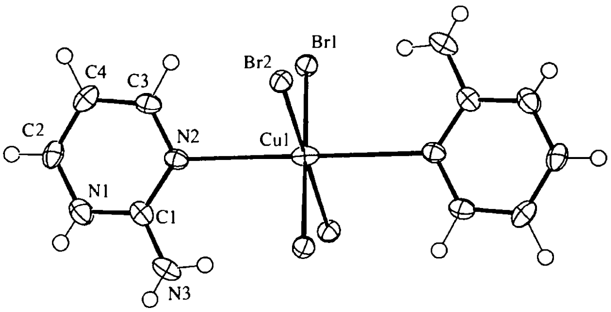


Fig. 1. A view of structure (I) showing the labelling of the non-H atoms. Displacement ellipsoids are shown at the 50% probability level for non-H atoms; H atoms are represented by spheres of arbitrary radii.

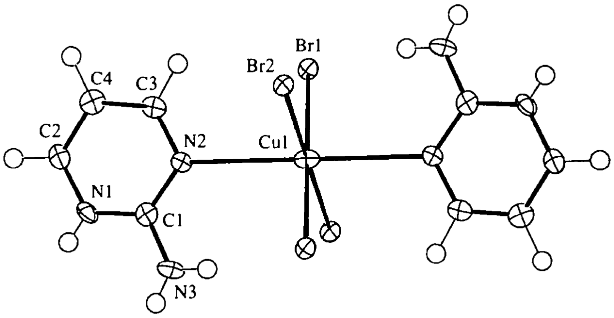


Fig. 2. A view of structure (II) showing the labelling of the non-H atoms. Displacement ellipsoids are shown at the 70% probability level for non-H atoms; H atoms are represented by spheres of arbitrary radii.

Experimental

The compound was synthesized by reaction of a suspension of 2-aminopyrimidine (2 g) in acetonitrile (40 ml) with a solution of $CuBr_2$ (2.35 g) in acetonitrile (30 ml), this latter solution being added dropwise to the first one, with slow stirring. Simultaneously, HBr (2 ml) was added. The mixture has a dark violet colour; after 1 h of stirring at 333 K, the solution was filtered off and allowed to crystallize. After 24 h, many plate-shaped bright and very dark-brown crystals appeared which were washed with *n*-pentane. The crystals were of suitable quality for X-ray structure analysis.

Structure (I)

Crystal data

$(C_4H_6N_3)_2[CuBr_4]$
$M_r = 575.42$
Monoclinic
$P2_1/c$
$a = 7.287\ (3)$ Å
$b = 13.779\ (4)$ Å
$c = 7.415\ (5)$ Å
$\beta = 99.55\ (10)°$
$V = 734.2\ (6)$ Å^3
$Z = 2$
$D_x = 2.603$ Mg m^{-3}
D_m not measured

Mo $K\alpha$ radiation
$\lambda = 0.71073$ Å
Cell parameters from 25 reflections
$\theta = 15–25°$
$\mu = 12.367$ mm^{-1}
$T = 200\ (2)$ K
Prismatic
0.33 × 0.26 × 0.26 mm
Brown

Data collection

Nonius CAD-4 diffractometer
$\omega–2\theta$ scans
Absorption correction: ψ scans (North, Phillips & Mathews, 1968)
$T_{\min} = 0.026$, $T_{\max} = 0.040$
3855 measured reflections
3207 independent reflections
1465 reflections with $I > 2\sigma(I)$

$R_{\rm int} = 0.070$
$\theta_{\max} = 34.96°$
$h = -11 \rightarrow 11$
$k = -2 \rightarrow 22$
$l = 0 \rightarrow 11$
3 standard reflections every 200 reflections frequency: 60 min intensity decay: 7.82%

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.050$
$wR(F^2) = 0.154$
$S = 0.995$
3207 reflections
101 parameters
H atoms refined isotropically
$w = 1/[\sigma^2(F_o^2) + (0.0709P)^2 + 0.4494P]$ where $P = (F_o^2 + 2F_c^2)/3$

$(\Delta/\sigma)_{\max} < 0.001$
$\Delta\rho_{\max} = 1.610$ e Å^{-3}
$\Delta\rho_{\min} = -1.607$ e Å^{-3}
Extinction correction: none
Scattering factors from *International Tables for Crystallography* (Vol. C)

Table 1. *Fractional atomic coordinates and equivalent isotropic displacement parameters (Å^2) for (I)*

$$U_{\rm eq} = (1/3)\Sigma_i\Sigma_j U^{ij} a_i^* a_j^* \mathbf{a}_i.\mathbf{a}_j.$$

	x	y	z	$U_{\rm eq}$
Br1	0.17226 (9)	0.05050 (5)	−0.24624 (9)	0.02000 (16)
Br2	0.25428 (9)	0.05717 (5)	0.22796 (9)	0.01922 (16)
Cu1	0	0	0	0.0198 (3)
N1	−0.2214 (9)	0.3411 (5)	0.0042 (9)	0.0261 (13)
N2	−0.1985 (7)	0.1709 (4)	−0.0133 (7)	0.0187 (11)
N3	0.0342 (9)	0.2675 (5)	−0.0864 (9)	0.0259 (13)
C1	−0.1289 (9)	0.2596 (5)	−0.0313 (8)	0.0188 (13)
C2	−0.3920 (9)	0.3357 (5)	0.0543 (9)	0.0231 (14)
C3	−0.3674 (9)	0.1659 (5)	0.0327 (10)	0.0232 (14)
C4	−0.4714 (9)	0.2468 (5)	0.0666 (9)	0.0222 (14)

Table 2. *Selected geometric parameters (Å, °) for (I)*

Br1—Cu1	2.481 (2)	Cu1—N2	2.757 (6)
Br2—Cu1	2.423 (2)	Br1—Br2$^{\rm i}$	4.042 (3)
Br2—Cu1—Br1	90.02 (5)		

Symmetry code: (i) $x, y, z - 1$.

Table 3. *Hydrogen-bonding geometry (Å, °) for (I)*

D—H$\cdots A$	D—H	H$\cdots A$	$D\cdots A$	D—H$\cdots A$
N3—H3$A\cdots$Br1	0.89 (4)	2.55 (4)	3.43 (1)	169 (3)
N3—H3$B\cdots$Br2$^{\rm i}$	0.73 (4)	2.61 (5)	3.32 (1)	168 (3)

Symmetry code: (i) $x, \frac{1}{2} - y, z - \frac{1}{2}$.

Structure (II)

Crystal data

$(C_4H_6N_3)_2[CuBr_4]$
$M_r = 575.42$
Monoclinic
$P2_1/c$
$a = 7.259\ (2)$ Å
$b = 13.757\ (4)$ Å
$c = 7.377\ (3)$ Å
$\beta = 99.87\ (3)°$
$V = 725.8\ (4)$ Å^3
$Z = 2$
$D_x = 2.633$ Mg m^{-3}
D_m not measured

Mo $K\alpha$ radiation
$\lambda = 0.71073$ Å
Cell parameters from 25 reflections
$\theta = 15–20°$
$\mu = 12.510$ mm^{-1}
$T = 100\ (2)$ K
Prismatic
0.33 × 0.26 × 0.26 mm
Brown

Data collection

Nonius CAD-4 diffractometer
$\omega–2\theta$ scans
Absorption correction: ψ scans (North, Phillips & Mathews, 1968)
$T_{\min} = 0.026$, $T_{\max} = 0.039$
3369 measured reflections
3175 independent reflections
1752 reflections with $I > 2\sigma(I)$

$R_{\rm int} = 0.054$
$\theta_{\max} = 34.96°$
$h = -11 \rightarrow 11$
$k = 0 \rightarrow 22$
$l = 0 \rightarrow 11$
3 standard reflections every 200 reflections frequency: 60 min intensity decay: 5.61%

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.042$
$wR(F^2) = 0.113$
$S = 1.004$
3175 reflections
107 parameters
H atoms refined isotropically
$w = 1/[\sigma^2(F_o^2) + (0.0507P)^2]$ where $P = (F_o^2 + 2F_c^2)/3$

$(\Delta/\sigma)_{\max} < 0.001$
$\Delta\rho_{\max} = 1.833$ e Å^{-3}
$\Delta\rho_{\min} = -1.296$ e Å^{-3}
Extinction correction: none
Scattering factors from *International Tables for Crystallography* (Vol. C)

Table 4. *Fractional atomic coordinates and equivalent isotropic displacement parameters (Å^2) for (II)*

$$U_{\rm eq} = (1/3)\Sigma_i\Sigma_j U^{ij} a_i^* a_j^* \mathbf{a}_i.\mathbf{a}_j.$$

	x	y	z	$U_{\rm eq}$
Br1	0.17217 (6)	0.05068 (4)	−0.24739 (6)	0.01063 (11)
Br2	0.25578 (6)	0.05693 (4)	0.22974 (6)	0.01038 (11)
Cu1	0	0	0	0.01109 (17)
N1	−0.2219 (6)	0.3407 (3)	0.0050 (7)	0.0133 (8)
N2	−0.1975 (6)	0.1698 (3)	−0.0126 (5)	0.0096 (8)
N3	0.0347 (6)	0.2680 (4)	−0.0866 (7)	0.0152 (9)
C1	−0.1287 (7)	0.2594 (4)	−0.0305 (6)	0.0110 (9)
C2	−0.3946 (7)	0.3350 (4)	0.0540 (7)	0.0130 (8)
C3	−0.3667 (7)	0.1647 (4)	0.0341 (7)	0.0119 (8)
C4	−0.4719 (7)	0.2457 (4)	0.0680 (7)	0.0130 (7)

Table 5. *Selected geometric parameters (Å, °) for (II)*

Br1—Cu1	2.482 (1)	Cu1—N2	2.734 (4)
Br2—Cu1	2.419 (1)	Br1—Br2'	4.007 (2)
Br2—Cu1—Br1	90.08 (3)		

Symmetry code: (i) $x, y, z - 1$.

Table 6. *Hydrogen-bonding geometry (Å, °) for (II)*

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
N3—H3*A*···Br1	0.94 (7)	2.50 (7)	3.43 (1)	170 (6)
N3—H3*B*···Br2'	0.77 (7)	2.58 (7)	3.31 (1)	162 (7)

Symmetry code: (i) $x, \frac{1}{2} - y, z - \frac{1}{2}$.

The structure was solved by Patterson and Fourier methods (Beurskens *et al.*, 1992). Non-H atoms were refined anisotropically by full-matrix least-squares techniques. Some of the H atoms were isotropically refined, others were geometrically calculated and refined riding with common isotropic displacement parameters in both structures. The final difference Fourier maps show several electron density peaks greater than 1 e Å^{-3}, for both structures, close to the Br and Cu atoms. A free anisotropic refinement of atom C3 in structure (II) leads to odd values for the principal axis of the thermal tensor, which are also affected by rounding off errors. Anisotropic refinement using similar parameters (*SIMU* in *SHELXL*93; Sheldrick, 1993) for all C atoms of the 2-aminopyrimidine leads to physically acceptable results. All calculations were made at the University of Oviedo on the Scientific Computer Center and X-ray group DEC/AXP computers

For both compounds, data collection: *CAD*-4 *EXPRESS* (Enraf–Nonius, 1994); cell refinement: *CRYSDA DIRDIF*; data reduction: *REFLEX* (local program); molecular graphics: *Xtal_GX* (Hall & Boulay, 1995). Geometrical calculations made with *PARST* (Nardelli, 1983); software used to prepare material for publication: *SHELXL*93.

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: NA1316). Services for accessing these data are described at the back of the journal.

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The 1:1 Antimony Trichloride Adduct of Chlorobis(2,6-dimethylpiperidin-1-yl)-phosphine Oxide

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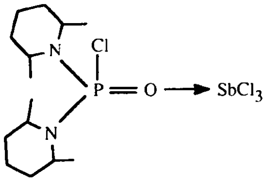
Abstract

In the structure of the title complex, $[(C_7H_{14}N)_2Cl\text{-}P(O)].SbCl_3$, the Sb atom shows a distorted trigonal bipyramidal geometry (including the lone pair). The O—Sb interaction of antimony with the phosphoryl O atom is only moderate and is weaker than that observed in the known compound $Cl_3PO \rightarrow SbCl_5$.

Comment

The phosphoryl unit in compounds of type $X_3P{=}O$ contains an electron-rich O atom that can act as a donor to metal centres (Burford, 1992). Several such complexes have been structurally characterized in which the angle at the phosphoryl O atom varies from 130 to 180° depending on the substituents and metal centres. Antimony trihalides can also act as weak acceptors (Pohl, Saak, Lotzand & Haase, 1990). In this paper, we report the synthesis and structure of the title compound $[(Me_2C_5H_8N)_2P(Cl)O] \rightarrow SbCl_3$, (2).



(2)