C112	0.6873 (5)	0.6564 (4)	0.3431 (2)	0.0534 (9)
C113	0.8339 (6)	0.7191 (4)	0.4163 (3)	0.0610 (10)
C114	0.8653 (5)	0.6540 (4)	0.4805 (3)	0.0593 (10)
C115	0.7489 (5)	0.5248 (4)	0.4724 (2)	0.0494 (8)
C116	0.7686 (6)	0.4486 (5)	0.5362 (3)	0.0620 (11)
C121	0.4776 (5)	0.3382 (3)	0.3832 (2)	0.0425 (7)
C122	0.2180 (6)	0.1721 (4)	0.2970 (3)	0.0559 (9)
C123	0.2284 (7)	0.0952 (4)	0.3577 (3)	0.0679 (11)
C124	0.3676 (7)	0.1412 (5)	0.4316 (3)	0.0693 (12)
C125	0.4994 (6)	0.2668 (4)	0.4470 (2)	0.0542 (9)
C126	0.6512 (7)	0.3274 (5)	0.5238 (3)	0.0682 (12)
C131	0.2464 (4)	0.2738 (3)	0.0449 (2)	0.0379 (7)
C132	−0.0005 (5)	0.2474 (4)	0.1125 (3)	0.0523 (9)
C133	−0.1190 (5)	0.1575 (4)	0.0353 (3)	0.0558 (9)
C134	−0.0512 (5)	0.1262 (4)	−0.0384 (3)	0.0544 (9)
C135	0.1366 (4)	0.1857 (3)	−0.0359 (2)	0.0428 (7)
C136	0.2209 (5)	0.1623 (4)	−0.1100 (3)	0.0556 (9)
C141	0.4382 (4)	0.3391 (3)	0.0518 (2)	0.0378 (7)
C142	0.7143 (5)	0.4841 (4)	0.1394 (2)	0.0503 (9)
C143	0.8017 (5)	0.4669 (4)	0.0691 (3)	0.0592 (10)
C144	0.7049 (5)	0.3824 (4)	−0.0111 (2)	0.0548 (9)
C145	0.5167 (4)	0.3148 (3)	−0.0219 (2)	0.0430 (7)
C146	0.4017 (5)	0.2223 (4)	−0.1037 (2)	0.0542 (9)
O100	0.1742 (4)	0.6516 (3)	0.7155 (2)	0.0734 (8)
N100	0.1715 (4)	0.7427 (3)	0.6791 (2)	0.0595 (8)
C100	0.2965 (5)	0.8619 (4)	0.7198 (2)	0.0511 (8)
C101	0.4286 (5)	0.8878 (4)	0.8004 (3)	0.0566 (9)
N101	0.5300 (5)	0.9044 (4)	0.8654 (3)	0.0812 (11)
C102	0.2905 (7)	0.9631 (5)	0.6775 (3)	0.0758 (12)
N102	0.2803 (8)	1.0415 (5)	0.6431 (4)	0.125 (2)

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

Cu1—N1	1.963 (3)	O100—N100	1.246 (4)
Cu1—N11	1.980 (3)	N100—C100	1.334 (5)
Cu1—N13	1.994 (3)	C100—C101	1.409 (5)
Cu1—N12	2.080 (3)	C100—C102	1.408 (6)
Cu1—N14	2.101 (3)	C101—N101	1.125 (5)
S1—C1	1.603 (4)	C102—N102	1.116 (6)
C1—N1	1.140 (4)		
N1—Cu1—N11	93.63 (13)	N12—Cu1—N14	116.21 (10)
N1—Cu1—N13	93.91 (12)	N1—C1—S1	178.2 (3)
N11—Cu1—N13	172.24 (11)	C1—N1—Cu1	171.1 (3)
N1—Cu1—N12	127.96 (12)	O100—N100—C100	117.3 (3)
N11—Cu1—N12	80.90 (12)	N100—C100—C101	123.0 (4)
N13—Cu1—N12	95.87 (12)	N100—C100—C102	116.2 (3)
N1—Cu1—N14	115.81 (12)	C101—C100—C102	120.8 (4)
N11—Cu1—N14	94.57 (11)	N101—C101—C100	177.5 (4)
N13—Cu1—N14	80.46 (11)	N102—C102—C100	178.0 (6)

Data collection and cell refinement were carried out using Syntex $P2_1$ software. Intensities were corrected for Lorentz and polarization factors using *XP*21 (Pavelčík, 1993). The structure was solved by direct methods using *XFPS* (Pavelčík, Rizzoli & Andreetti, 1990) and subsequent Fourier syntheses using *SHELXL*93 (Sheldrick, 1993). Anisotropic displacement parameters were refined for all non-H atoms. All H-atoms were located from difference Fourier maps and refined with isotropic displacement factors fixed to 0.05 Å^2. Geometrical analysis was performed using *PARST* (Nardelli, 1983) and *SHELXL*93. *ORTEP* (Johnson, 1965) was employed to draw the structure.

The authors thank Mrs Danková for help with the synthetic work.

Lists of structure factors, anisotropic displacement parameters, H-atom coordinates and bond distances and angles involving non-H atoms have been deposited with the IUCr (Reference: KA1099). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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Bis(4-bromopyrazole)dichlorocopper(II)

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Abstract

The structure consists of *trans*-square-planar [$CuCl_2(C_3H_3BrN_2)_2$] units linked through Cu···Cl bonds giving each Cu^{II} atom [4 + 2] coordination.

Comment

This report extends work on metal coordination of halogenated nitrogen ligands (Valle, Sánchez González & Ettorre, 1991, 1993; Casellato, Graziani, Peruzzo & Plazzogna, 1994). The title structure, (I), consists of *trans*-square-planar [$CuCl_2(C_3H_3BrN_2)_2$] units linked through Cu···Cl bonds giving each Cu^{II} atom [4 + 2] coordination. The molecules form chains along the [100] direction by doubling-chloride bridging. The bonding

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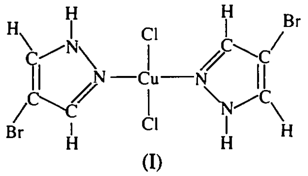

(I)

network is similar to that in dichlorobis(pyridine)copper(II) (Morosin, 1975). The closest contact between halogens is Br···Cl($x+1, y, z+1$) of 3.588 (3) Å. The range 3.12–3.62 Å can be calculated from the van der Waals radii of Br and Cl atoms bonded to C atoms (Nyburg & Faerman, 1985). The dihedral angle between the planes through N(1), N(2), C(3), C(4) and C(5), and Cu, N(2) and Cl is 14.1(2)°. This conformation is related to intramolecular N···Cl hydrogen bonding.

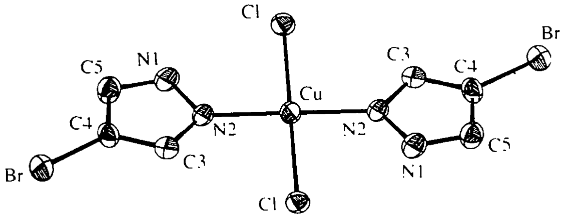

Fig. 1. *ORTEP*II plot (Johnson, 1976) of the title molecule [$CuCl_2(C_3H_3BrN_2)_2$]. Displacement ellipsoids are plotted at the 50% probability level.

Experimental

A 1:2 mixture of $CuCl_2$ and $C_3H_3BrN_2$ in hydrochloric acid was evaporated to dryness. Recrystallization from acetone–water gave [$CuCl_2(C_3H_3BrN_2)_2$].

Crystal data

[$CuCl_2(C_3H_3BrN_2)_2$]
$M_r = 428.4$
Monoclinic
$P2_1/c$
$a = 3.851$ (1) Å
$b = 15.077$ (2) Å
$c = 9.990$ (2) Å
$\beta = 95.2$ (1)°
$V = 577.6$ (2) Å^3
$Z = 2$
$D_x = 2.46$ Mg m^{-3}

Mo $K\alpha$ radiation
$\lambda = 0.71073$ Å
Cell parameters from 25 reflections
$\theta = 7$–12°
$\mu = 9.19$ mm^{-1}
Room temperature
Needle
0.5 × 0.1 × 0.1 mm
Green

Data collection

Philips PW1100 diffractometer
$\theta/2\theta$ scans
Absorption correction: none
1462 measured reflections
1385 independent reflections
833 observed reflections [$F > 3\sigma(F)$]
$R_{\rm int} = 0.057$

$\theta_{\rm max} = 28°$
$h = -5 \rightarrow 5$
$k = 0 \rightarrow 19$
$l = 0 \rightarrow 13$
3 standard reflections monitored every 50 reflections
intensity decay: 10%
intensity correction: none

Refinement

Refinement on F
$R = 0.048$
$wR = 0.048$
$S = 0.71$
833 reflections
82 parameters
H atoms refined isotropically
$w = 1/[\sigma^2(F) + 0.00436F^2]$
$(\Delta/\sigma)_{\rm max} = 0.361$

$\Delta\rho_{\rm max} = 1.34$ e Å^{-3}
$\Delta\rho_{\rm min} = -1.30$ e Å^{-3}
Extinction correction: none
Atomic scattering factors from *International Tables for X-ray Crystallography* (1974, Vol. IV) and *SHELX*76 (Sheldrick, 1976)

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

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

	x	y	z	$U_{\rm eq}$
Cu	0	0	0	0.0285 (4)
Br	0.3083 (2)	0.14381 (7)	0.55374 (9)	0.0423 (3)
Cl	−0.4151 (5)	0.0988 (1)	−0.1002 (2)	0.0303 (6)
N(1)	−0.091 (2)	0.1574 (5)	0.1694 (7)	0.036 (2)
N(2)	0.037 (2)	0.0734 (4)	0.1664 (6)	0.027 (2)
C(3)	0.181 (2)	0.0585 (5)	0.2914 (8)	0.033 (3)
C(4)	0.152 (2)	0.1314 (6)	0.3722 (8)	0.031 (3)
C(5)	−0.027 (2)	0.1949 (5)	0.2907 (8)	0.035 (3)

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

Cu—Cl	2.342 (2)	Cu—N(2)	1.991 (6)
N(1)—N(2)	1.359 (10)	N(2)—C(3)	1.339 (10)
C(3)—C(4)	1.375 (11)	N(1)—C(5)	1.339 (11)
C(4)—C(5)	1.399 (11)	C(4)—Br	1.867 (8)
Cu···Cl$^{\rm i}$	2.950 (3)	N(1)···Cl	2.998 (7)
Cl—Cu—N(2)	89.8 (2)	Cl—Cu—Cl$^{\rm i}$	87.3 (1)
N(2)—Cu—Cl$^{\rm i}$	89.8 (2)	Cu—N(2)—N(1)	122.5 (5)
Cu—N(2)—C(3)	132.6 (5)	N(2)—N(1)—C(5)	112.1 (7)
N(1)—N(2)—C(3)	104.9 (6)	N(2)—C(3)—C(4)	111.3 (7)
C(3)—C(4)—C(5)	105.5 (7)	N(1)—C(5)—C(4)	106.1 (7)
C(3)—C(4)—Br	127.9 (6)	C(5)—C(4)—Br	126.5 (6)

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

Data collection, cell refinement and data reduction were carried out using local programs. The structure was solved by direct methods using *SIR*92 (Altomare, Cascarano, Giacovazzo & Guagliardi, 1993) and refined using *SHELX*76 (Sheldrick, 1976). Other calculations were performed usng *PARST* (Nardelli, 1983). Molecular graphics were produced using *ORTEP*II (Johnson, 1976).

Lists of structure factors, anisotropic displacement parameters, H-atom coordinates and complete geometry have been deposited with the IUCr (Reference: NA1136). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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Acta Cryst. (1995). C**51**, 1295–1297

Aluminium Cupferronate, [Al(C$_6$H$_5$N$_2$O$_2$)$_3$]

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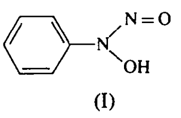
Abstract

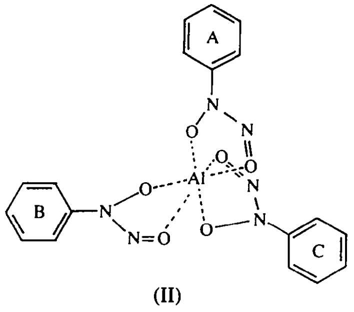
The Al ion in tris(*N*-nitroso-*N*-phenylhydroxylaminato)aluminium(III), [Al(C$_6$H$_5$N$_2$O$_2$)$_3$], has distorted octahedral coordination defined by six O atoms from three chelate ligands [Al—O = 1.875 (4)–1.894 (4) Å]. In each ligand the phenyl ring nearly coincides with the plane of the nitrosohydroxylaminato group.

Comment

N-Nitroso compounds, such as dimethylnitrosoamine and *N*-nitrosourea are known carcinogens (Nishimura *et al.*, 1985; Ishii, Tatsuta, Baba, Uehara & Nakaizumi, 1994). In order to clarify the cytotoxicity of *N*-nitroso compounds, it is important to accumulate precise structural data concerning the interaction modes of *N*-nitroso compounds with biomaterials. Accordingly, the crystal structure of the Al^{III} complex of deprotonated cupferron, (I), tris(*N*-nitrosophenylhydroxylaminato)aluminium(III), (II), has been determined. The structures of the related complexes iron cupferronate (van der Helm, Merritt & Degeilh, 1965) and (*N*-nitrosophenylhydroxylamininato-*O*,*O*′)bis(triphenylphosphine)copper(I) (Charlambous, Haines, Harris, Hendrick & Taylor, 1984) have been reported.



(I)



(II)

The molecular structure is illustrated in Fig. 1. The three cupferronato ligands *A*, *B* and *C* are asymmetrically attached to the Al^{3+} ion. In each ligand, the phenyl ring is nearly coplanar with the plane of the nitrosohydroxylaminato group, although the N—N—C—C torsion angles [N(2*A*)—N(1*A*)—C(1*A*)—C(6*A*) = 2.1 (8), N(2*B*)—N(1*B*)—C(1*B*)—C(6*B*) = −9.0 (9), N(2*C*)—N(1*C*)—C(1*C*)—C(6*C*) = −16 (1)°] show some variation. The Al^{3+} ion has distorted octahedral coordination defined by six O atoms from three ligands with similar O atoms meridional [O(1*A*)—Al(1)—O(1*C*) = 168.1 (2), O(1*B*)—Al(1)—O(2*A*) = 167.6 (2), O(2*B*)—Al(1)—O(2*C*) = 166.0 (2)°]. Although distances and angles within the phenyl rings are unexceptional, physically unreasonable displacement parameters of some phenyl C atoms (Fig. 1 and Table 1) and the high final *R* value are consistent with some positional disorder of the phenyl rings.

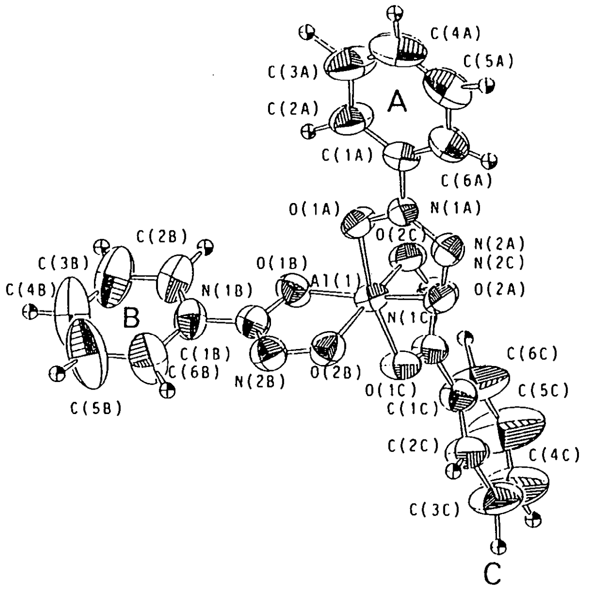


Fig. 1. *ORTEP*II (Johnson, 1976) view of (II) showing the atom-labelling scheme. Displacement ellipsoids are plotted at the 50% probability level.

Experimental

Crystals were obtained by slow evaporation at room temperature of solutions in 50% ethanol. The density D_m was measured by flotation in C$_6$H$_6$–CCl$_4$.

Crystal data

[Al(C$_6$H$_5$N$_2$O$_2$)$_3$]
$M_r = 438.33$
Monoclinic
$P2_1/n$
$a = 11.119\ (6)$ Å
$b = 16.062\ (3)$ Å
$c = 12.027\ (4)$ Å
$\beta = 100.72\ (3)°$

Mo $K\alpha$ radiation
$\lambda = 0.71069$ Å
Cell parameters from 25 reflections
$\theta = 10.15–11.75°$
$\mu = 0.137$ mm^{-1}
$T = 296$ K
Plate

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