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$[CuL_2][ClO_4]$ and $[AgL_2][BF_4]$, where L = 6,6′-Dibromo-2,2′-bipyridine

Michael D. Ward, Samantha M. Couchman and John C. Jeffery

School of Chemistry, University of Bristol, Cantock's Close, Bristol BS8 1TS, England. E-mail: mike.ward@bristol.ac.uk

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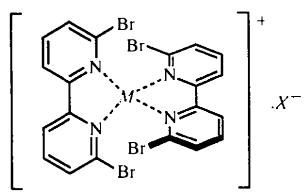
Abstract

The complexes bis(6,6′-dibromo-2,2′-bipyridine-*N*,*N*′)copper(I) perchlorate, $[Cu(C_{10}H_6Br_2N_2)_2]ClO_4$, and bis(6,6′-dibromo-2,2′-bipyridine-*N*,*N*′)silver(I) tetrafluoroborate, $[Ag(C_{10}H_6Br_2N_2)_2]BF_4$, both contain four-coordinate pseudo-tetrahedral metal centres, in which the two bidentate chelating ligands are nearly mutually perpendicular; the average dihedral angle between the two MN_2 planes is 87.9° for M = Cu but only 75° for M = Ag, which reflects the lesser inter-ligand steric interactions in the silver(I) complex, arising from the greater metal–ligand bond distances. For both complexes, the crystal packing is dominated by intermolecular Br· · ·Br interactions.

Comment

Four-coordinate mononuclear copper(I) complexes of the type $Cu(NN)_2$, where *NN* denotes a derivative of 2,2′-bipyridine or 1,10-phenanthroline, have been of interest for their photophysical and electrochemical properties, and in particular the relationship between these properties and the extent of distortion of the complexes away from D_{2d} symmetry (in which the two bidentate ligands are mutually perpendicular) towards D_{4h} (in which they are coplanar) (Cargill Thompson *et al.*, 1997; Müller *et al.*, 1996; Bardwell *et al.*, 1996; Geoffroy *et al.*, 1990; Federlin *et al.*, 1990). The pseudo-tetrahedral D_{2d} geometry can be favoured by attachment of bulky substituents (commonly aryl or alkyl) to the C atoms adjacent to the N donor atoms (*i.e.* C6 and C6′ on a 2,2′-bipyridyl core, or C2 and C9 on a 1,10-phenanthroline core). Such substituents can favour pseudo-tetrahedral geometries by forming 'interlocked' structures with favourable inter-ligand interactions, and actively disfavour planar geometries for steric reasons. In contrast, complexes of this type with silver(I) are much rarer (Cargill Thompson *et al.*, 1997; Goodwin *et al.*, 1986). We describe here the crystal structures of the copper(I) and silver(I) complexes of 6,6′-dibromo-2,2′-bipyridine [(1) and (2), respectively], which should impose pseudo-tetrahedral geometry because of the bulky Br-atom substituents. These are the first crystal structures of complexes with this ligand to be reported.



(1) M = Cu; X = ClO_4
(2) M = Ag; X = BF_4

Reaction of L with $[Cu(MeCN)_4][PF_6]$ in methanol in a 2:1 ratio afforded $[CuL_2][PF_6]$ as an orange solid; a small amount was converted to the perchlorate salt for crystallization, and X-ray quality crystals were grown from a dichloromethane/hexane mixture. The structure of $[CuL_2][ClO_4]$ is rather unusual in that it contains three crystallographically independent formula units in the asymmetric unit. One of the independent complex cations is shown in Fig. 1; the other two are very similar. The atom-numbering scheme is the same for all three complex units, with the first digit (1, 2 or 3) denoting the complex unit. In all three complex cations, the Cu—N distances lie in the range 2.02–2.06 Å, with the usual distortion from regular tetrahedral geometry arising from the restricted bite angles of the chelating fragments (*ca* 80°). The dihedral angles between the two CuN_2 planes are 85.8 (2), 88.6 (2) and 89.4 (2)° for complex units 1, 2 and 3, respectively. The ligands are therefore virtually perpendicular to one another in each case, which may be ascribed to the steric bulk of the Br atoms; with less bulky substituents in the same positions, the angle between the two CuN_2 planes is usually compressed to 70–80° in the crystals as a consequence of packing forces (Goodwin *et al.*, 1986; Ichinaga *et al.*, 1987). Apart from this, the geometries of the $[CuL_2]^+$ fragments are generally similar to those of related complexes with substituted diimine-based ligands (Cargill Thompson *et al.*, 1997; Müller *et al.*, 1996; Bardwell *et al.*, 1996; Geoffroy *et al.*, 1990; Federlin *et al.*, 1990).

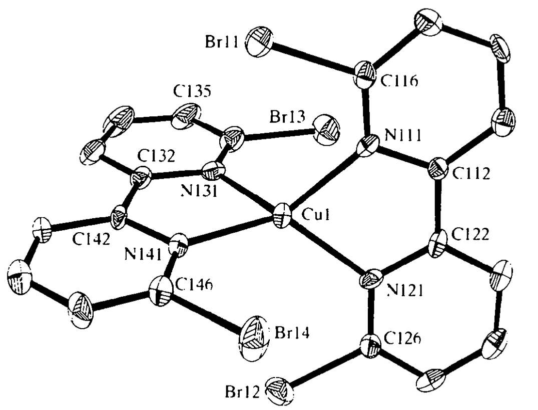


Fig. 1. The structure of one of the independent complex cations of $[CuL_2][ClO_4]$. Displacement ellipsoids are plotted at the 40% probability level.

The crystal packing is dominated by a network of intermolecular Br···Br contacts, most of which are significantly shorter than the sum of the van der Waals radii (*ca* 3.9 Å for two Br atoms). The following such contacts were identified: Br34···Br24($1-x$, $1-y$, $1-z$) 3.681 (5), Br34···Br22 3.552 (5), Br33···Br21($x-1$, y, z) 3.595 (5), Br31···Br11($x-1$, $y-1$, z) 3.697 (5), Br22···Br13($1-x$, $1-y$, $-z$) 3.651 (5), Br12···Br12($1-x$, $2-y$, $-z$) 3.573 (5) and Br11···Br11($2-x$, $2-y$, $-z$) 3.465 (5) Å. In addition, the following intermolecular contacts are only slightly above the sum of the van der Waals radii: Br32···Br24($1-x$, $1-y$, $1-z$) 4.190 (5), Br31···Br14($x-1$, $y-1$, z) 4.058 (5) and Br23···Br13($1-x$, $1-y$, $-z$) 4.087 (5) Å. A fragment of the lattice emphasizing these interactions is shown in Fig. 2.

Halogen–halogen interactions of this nature are well known in crystals (Pedireddi *et al.*, 1994) and have been exploited in crystal engineering (Desiraju, 1995); in the case of Br···Br contacts, a wide angular variation can occur with no clearly defined preference for any particular geometry (Pedireddi *et al.*, 1994). The network of Br···Br contacts appears to preclude any aromatic π-stacking interactions between complex units.

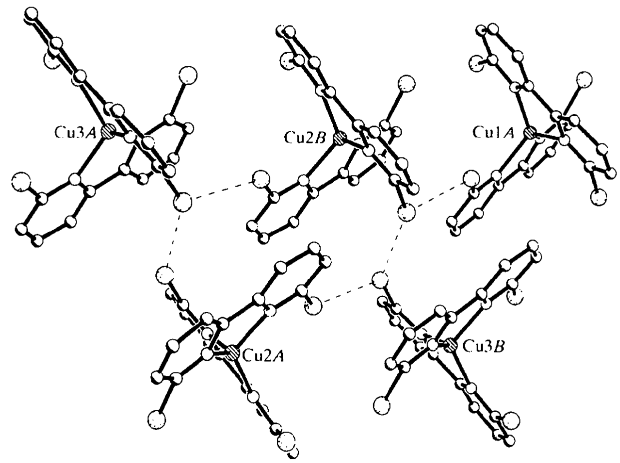


Fig. 2. Part of the crystal packing in $[CuL_2][ClO_4]$ emphasizing the network of non-bonded Br···Br interactions.

Reaction of L with $AgBF_4$ in MeOH in a ratio of 2:1 afforded $[AgL_2][BF_4]$, which yielded X-ray quality crystals from dichloromethane. The crystal structure (Fig. 3) shows the expected pseudo-tetrahedral structure, basically similar to that of the copper(I) complex above. The Ag—N distances are in the usual range of 2.30–2.37 Å; the longer metal–ligand distances compared with the copper(I) complex mean that inter-ligand steric factors are somewhat relaxed, as shown by the greater degree of compression of the angle between the two AgN_2 planes, which is 75°. The molecules are arranged in columns in the crystal, with short intermolecular Br···Br contacts [Br11···Br22(x, $\frac{1}{2}-y$, $\frac{1}{2}+z$) 3.613 (3) Å] between molecules along the column. Additional, weaker, intermolecular Br···Br interactions are: Br12···Br22(x, $\frac{1}{2}-y$, $-\frac{1}{2}+z$) 4.069 (3) and Br21···Br21($2-x$, $-y$, $2-z$) 3.973 (3) Å. There is also an interaction with the tetrafluoroborate anions: Br12···F4(x, $\frac{1}{2}-y$, $-\frac{1}{2}+z$) 3.211 (5) Å. Again, there are no close aromatic π-stacking interactions between complex units.

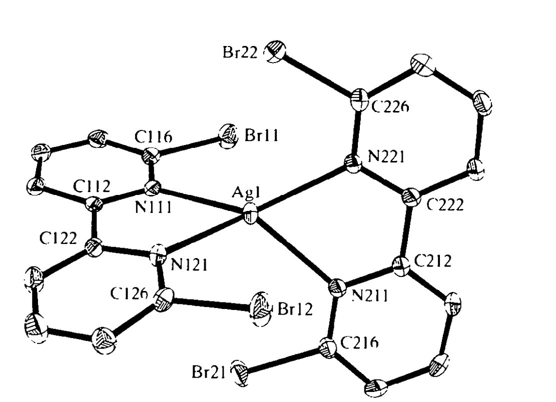


Fig. 3. The structure of the complex cation of $[AgL_2][BF_4]$. Displacement ellipsoids are plotted at the 40% probability level.

Experimental

The title complexes were prepared by stirring a mixture of *L* with either $[Cu(MeCN)_4][PF_6]$ or $AgBF_4$ in a 2:1 ratio in methanol at room temperature for 1 h. Concentration of the mixture and cooling resulted in precipitation of the product as a microcrystalline solid (orange or pale yellow, respectively) in 80–90% yield. X-ray quality crystals of $[AgL_2][BF_4]$ were grown by slow evaporation of a concentrated dichloromethane solution of the complex. A small amount of $[CuL_2][PF_6]$ was converted to $[CuL_2][ClO_4]$ by addition of aqueous $NaClO_4$ to an acetonitrile solution of the hexafluorophosphate salt, and was crystallized from dichloromethane/hexane. For $[CuL_2][PF_6]$, analysis found: C 28.4, H 1.4, N 6.5%; $C_{20}H_{12}Br_4CuF_6N_4P$ requires: C 28.7, H 1.5, N 6.7%. FAB MS: m/z = 691, $\{CuL_2\}^+$; 377, $\{CuL\}^+$. For $[AgL_2][BF_4]$, analysis found: C 29.4, H 1.3, N 6.8%; $C_{20}H_{12}AgBBr_4F_4N_4$ requires: C 29.2, H 1.5, N 6.8%. FAB MS: m/z = 735, $\{AgL_2\}^+$; 421, $\{AgL\}^+$.

Compound (1)

Crystal data

$[Cu(C_{10}H_6Br_2N_2)_2]ClO_4$
M_r = 790.97
Triclinic
$P\bar{1}$
a = 13.971 (2) Å
b = 14.308 (3) Å
c = 18.205 (4) Å
α = 93.241 (14)°
β = 98.320 (15)°
γ = 92.942 (12)°
V = 3588.6 (11) Å^3
Z = 6
D_x = 2.196 Mg m^{-3}
D_m not measured

Mo $K\alpha$ radiation
λ = 0.71073 Å
Cell parameters from 160 reflections
θ = 2.2–27.4°
μ = 7.742 mm^{-1}
T = 173 (2) K
Plate
0.30 × 0.20 × 0.05 mm
Orange

Data collection

Siemens SMART area-detector diffractometer
ω rotation scans with narrow frames
Absorption correction: ψ scan (*SADABS*; Sheldrick, 1996)
T_{min} = 0.12, T_{max} = 0.70
36 286 measured reflections

16 137 independent reflections
7620 reflections with $I > 2\sigma(I)$
R_{int} = 0.070
θ_{max} = 27.49°
h = −18 → 18
k = −18 → 18
l = −23 → 22

Refinement

Refinement on F^2
$R(F)$ = 0.050
$wR(F^2)$ = 0.070
S = 1.021
16 137 reflections
947 parameters
H atoms: see below
$w = 1/[\sigma^2(F_o^2) + (0.0189P)^2]$ where $P = (F_o^2 + 2F_c^2)/3$

$(\Delta/\sigma)_{max}$ = 0.001
$\Delta\rho_{max}$ = 0.663 e Å^{-3}
$\Delta\rho_{min}$ = −0.706 e Å^{-3}
Extinction correction: none
Scattering factors from *International Tables for Crystallography* (Vol. C)

Table 1. *Selected geometric parameters (Å, °) for (1)*

Cu1—N141	2.021 (5)	Cu2—N221	2.040 (5)
Cu1—N121	2.035 (5)	Cu2—N241	2.054 (5)
Cu1—N111	2.036 (5)	Cu3—N321	2.022 (5)
Cu1—N131	2.058 (5)	Cu3—N341	2.029 (5)
Cu2—N231	2.019 (5)	Cu3—N331	2.048 (5)
Cu2—N211	2.033 (5)	Cu3—N311	2.052 (5)
N141—Cu1—N121	131.4 (2)	N231—Cu2—N241	80.2 (2)
N141—Cu1—N111	130.7 (2)	N211—Cu2—N241	121.9 (2)
N121—Cu1—N111	80.7 (2)	N221—Cu2—N241	116.2 (2)
N141—Cu1—N131	79.9 (2)	N321—Cu3—N341	129.3 (2)
N121—Cu1—N131	123.5 (2)	N321—Cu3—N331	132.3 (2)
N111—Cu1—N131	116.0 (2)	N341—Cu3—N331	81.2 (2)
N231—Cu2—N211	133.8 (2)	N321—Cu3—N311	81.1 (2)
N231—Cu2—N221	128.5 (2)	N341—Cu3—N311	118.4 (2)
N211—Cu2—N221	80.9 (2)	N331—Cu3—N311	119.4 (2)

Compound (2)

Crystal data

$[Ag(C_{10}H_6Br_2N_2)_2]BF_4$
M_r = 822.66
Monoclinic
$P2_1/c$
a = 12.726 (2) Å
b = 22.233 (3) Å
c = 8.6069 (8) Å
β = 97.437 (12)°
V = 2414.8 (5) Å^3
Z = 4
D_x = 2.263 Mg m^{-3}
D_m not measured

Mo $K\alpha$ radiation
λ = 0.71073 Å
Cell parameters from 336 reflections
θ = 2.5–26.9°
μ = 7.502 mm^{-1}
T = 173 (2) K
Prism
0.40 × 0.20 × 0.15 mm
Colourless

Data collection

Siemens SMART area-detector diffractometer
ω rotation scans with narrow frames
Absorption correction: ψ scan (*SADABS*; Sheldrick, 1996)
T_{min} = 0.24, T_{max} = 0.33
15 061 measured reflections

5494 independent reflections
4094 reflections with $I > 2\sigma(I)$
R_{int} = 0.035
θ_{max} = 27.49°
h = −11 → 16
k = −27 → 28
l = −11 → 10

Refinement

Refinement on F^2
$R(F)$ = 0.031
$wR(F^2)$ = 0.062
S = 1.022
5494 reflections
308 parameters
H atoms: see below
$w = 1/[\sigma^2(F_o^2) + (0.0308P)^2]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max}$ = −0.002

$\Delta\rho_{max}$ = 1.286 e Å^{-3}
$\Delta\rho_{min}$ = −1.000 e Å^{-3}
Extinction correction: *SHELXTL* (Siemens, 1995*a*)
Extinction coefficient: 0.00319 (11)
Scattering factors from *International Tables for Crystallography* (Vol. C)

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

Ag1—N221	2.297 (3)	Ag1—N121	2.331 (3)
Ag1—N111	2.326 (3)	Ag1—N211	2.370 (3)
N221—Ag1—N111	136.57 (10)	N221—Ag1—N211	70.16 (10)
N221—Ag1—N121	137.67 (10)	N111—Ag1—N211	136.52 (10)
N111—Ag1—N121	70.67 (10)	N121—Ag1—N211	115.03 (10)

For both data sets, unit-cell dimensions were determined from reflections taken from three sets of 30 frames (at 0.3° steps in ω), each at 20 s exposure. Slightly more than a full hemisphere of reciprocal space was scanned by 0.3° ω steps at φ = 0, 90 and 180°, with the area detector held at $2\theta = -29°$ and each frame exposed for 30 s. The crystal-to-detector distance was 4.94 cm. Crystal decay was monitored by repeating the initial 50 frames at the end of data collection and analysing the duplicate reflections. No decay was observed in either data set. The data sets were corrected emprically for absorption effects and refined by the full-matrix least-squares method on all F^2 data. H atoms were constrained to idealized geometries and each was assigned an isotropic displacement parameter of 1.2 times the U_{eq} value of the attached atom. For [CuL_2]-[ClO_4], one of the three independent perchlorate anions is disordered. Atoms Cl1 and O14 were fixed, but rotational disorder about this bond resulted in atoms O11, O12 and O13 being each disordered over two sites in a 60:40 ratio. Three of these disordered atom sites (O12, O12′ and O13′) have rather extreme anisotropic displacement paramaters. For [AgL_2][BF_4], the largest residual electron-density peak of 1.29 e Å^{-3} is located 1.00 Å from Br21.

For both compounds, data collection: *SMART* (Siemens, 1995*b*); cell refinement: *SAINT* (Siemens, 1995*b*); data reduction: *SAINT*; program(s) used to solve structures: *SHELXTL* (Siemens, 1995*a*); program(s) used to refine structures: *SHELXTL*; molecular graphics: *SHELXTL*; software used to prepare material for publication: *SHELXTL*.

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: NA1374). Services for accessing these data are described at the back of the journal.

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Acta Cryst. (1998). C**54**, 1823–1825

Aquabis(2,3-butanedione dioximato-*N*,*N*′)-(cyclopentyl)cobalt(III)

YING CHEN, HUI-LAN CHEN, CHUN-YING DUAN AND YONG-JIANG LIU

Department of Chemistry, Coordination Chemistry Institute & State Key Laboratory of Coordination Chemistry, Nanjing University, Nanjing 210093, People's Republic of China. E-mail: hlchen@nju.edu.cn

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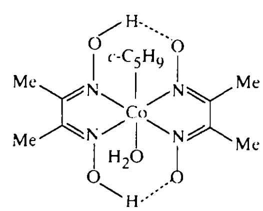
Abstract

The crystal structure determination of the title compound, a model for coenzyme B_{12}, indicates that it is [Co($C_4H_6N_2O_2$)(C_5H_9)($C_4H_8N_2O_2$)(H_2O)], *i.e.* one 2,3-butanedione dioxime ligand is neutral and the second is a dianion, with the Co^{III} ion in a distorted octahedral environment. The axial Co—C bond length [2.029 (2) Å] is close to that of coenzyme B_{12} [2.00 (1) Å].

Comment

Alkylcobaloximes [RCo(DH)$_2L$; where DH is the monoanion of dimethylglyoxime (2,3-butanedione dioxime), R is alkyl and L is a donor ligand] are a type of widely studied coenzyme B_{12} models having a σ-type Co—C bond; their structures and properties have been well characterized (Bresciani-Pahor *et al.*, 1985). However, only a few structures of alkylaquacobaloximes (L = H_2O) are available and in this paper, we report a new one, that of aquabis(2,3-butanedione dioximato-*N*,*N*′)(cyclopentyl)cobalt(III), (I).



(I)

An *ORTEP* plot (Johnson, 1965) of the title compound with the atom-numbering scheme is shown in Fig. 1. The Co^{III} ion is coordinated by four N atoms (N1, N2, N3 and N4), a C atom (C1′) and an O atom (O1*W*), forming a distorted octahedral environment. The four N atoms are coplanar. The Co^{III} atom is displaced slightly [0.030 (1) Å] from the N_4 mean plane towards the cyclopentyl group. The dihedral angle between the plane formed by atoms C1–C4, N1, N2, O1, O2 and Co1 (mean deviation from the