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A Topologically Novel Binuclear Silver Complex of Di-2-pyridyl Sulfide

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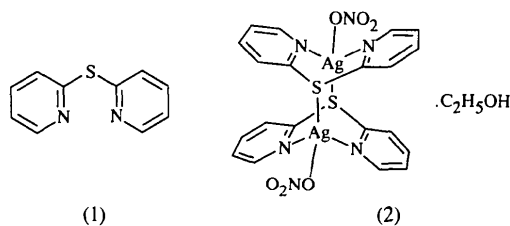
(Received 22 September 1997; accepted 30 October 1997)

Abstract

The reaction of di-2-pyridyl sulfide with silver nitrate produces a centrosymmetric binuclear complex, bis(di-2-pyridyl sulfide-*N,N'*:*S*)bis(nitrato-*O*)-disilver(I) ethanol solvate, $[\text{Ag}_2(\text{C}_{10}\text{H}_8\text{N}_2\text{S})_2(\text{NO}_3)_2] \cdot \text{C}_2\text{H}_5\text{OH}$, within which each Ag atom is coordinated to a monodentate nitrate, an S atom of one ligand and two N atoms of a second ligand. Topologically, this represents the first coordination analogue of the well known photodimers of anthracene.

Comment

During the course of a comprehensive study of the transition metal complexes of chelating heterocyclic ligands, we have investigated the reaction of di-2-pyridyl sulfide, (1), with silver nitrate. Recrystallization of this reaction product from ethanol afforded colourless crystals of a 1:1 metal–ligand stoichiometry, the structure of which we now report. The complex formed is a topologically novel binuclear complex, (2), wherein the ligand displays a mode of coordination not observed previously.



The complex crystallizes in the triclinic space group $P\bar{1}$, the asymmetric unit of which comprises an Ag atom chelated to the two N atoms of the ligand and to a monodentate nitrate anion, along with half a molecule of a disordered ethanol solvate. In addition, the Ag atom is coordinated to the S atom of a second ligand, related by a centre of inversion. This results in the assembly of a centrosymmetric binuclear complex (Fig. 1). Although many complexes of (1) have been described (Summers, 1987; Tresoldi *et al.*, 1991), this is the first complex involving coordination of the S atom of the ligand, presumably as a consequence of the thiophilic nature of Ag^{I} .

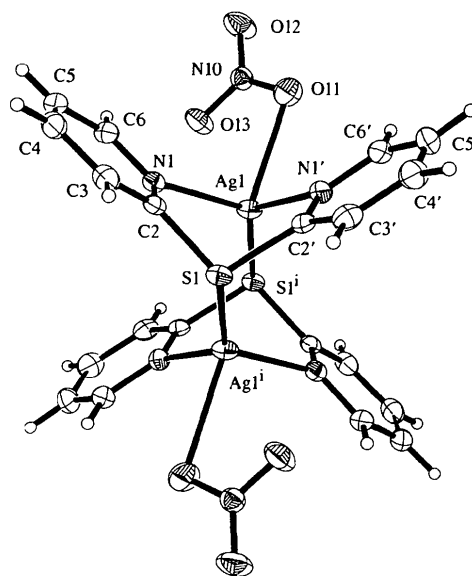


Fig. 1. Perspective view and atom labelling of the binuclear complex (2). Displacement ellipsoids are drawn at the 50% probability level and H atoms are drawn as small circles of arbitrary radii. [Symmetry code: (i) $1 - x, -y, 2 - y$.]

The six-membered chelate ring exists in a boat conformation, wherein the Ag and S atoms lie 1.057 (1) and 0.974 (1) Å, respectively, above the plane defined by N1, C2, N1' and C2'. A search of the Cambridge Structural Database (Allen & Kennard, 1993) retrieved five X-ray structures of complexes of (1) in which the ligand is chelated through the two N atoms: three Pd^{II} complexes (Tresoldi *et al.*, 1992; De Munno *et al.*, 1993; Nicolo *et al.*, 1996), one V^{IV} complex (Kondo *et al.*, 1995) and one Ru^{II} complex (Bruno *et al.*, 1995). In the

more stereorigid palladium and ruthenium complexes, the bite angles of the ligand [N1—M—N1' = 88.5–88.9°] are significantly greater than in the present case [N1—Ag1—N1' = 83.6(1)°] and the conformations of the chelate rings are somewhat more flattened boats. In the vanadium complex, both the ring conformation and bite angle [82.8(1)°] are similar to those in the silver complex.

The overall topology of the dimeric complex is interesting and novel in that it consists of a central prismatic core from which four pyridine rings extend. We believe that this is the first structurally characterized coordination compound to possess this arrangement, which bears a close resemblance to the well known face-to-face 9,9',10,10'-bridged photodimers of anthracene (Abboud *et al.*, 1990) and related organic molecules (Ando *et al.*, 1995). Furthermore, the fact that the Ag1...Ag1A [2.9954(3) Å] separation is considerably shorter than the S1...S1A [5.086(1) Å] distance produces a distortion to this general topology that has been observed in a transannularly-bridged derivative of an anthracene dimer (Herges *et al.*, 1994). In the silver complex, the planes of the two pyridine rings of the ligand are inclined at an angle of 75.1(2)°, which is substantially greater than the corresponding angle [44.8(3)°] between the planes of the two benzene rings in the anthracene photodimer.

The molecular packing is controlled by a linear hydrogen bond between the OH group of the disordered ethanol solvate and the O12 atom of the nitrate anion.

Experimental

Di-2-pyridyl sulfide, (1), was prepared according to the literature method of Chachaty *et al.* (1976). Complex (2) was prepared by reaction of an aqueous methanolic solution of silver nitrate with a methanol solution of (1). The resulting product was recrystallized from ethanol.

Crystal data

[Ag₂(C₁₀H₈N₂S)₂(NO₃)₂].-
C₂H₆O

M_r = 762.32

Triclinic

*P*1

a = 7.5131(1) Å

b = 9.1074(2) Å

c = 9.8983(2) Å

α = 83.786(1)°

β = 79.879(1)°

γ = 77.383(1)°

V = 648.93(2) Å³

Z = 1

D_x = 1.951 Mg m⁻³

D_m not measured

Mo *K*α radiation

λ = 0.71073 Å

Cell parameters from 6563 reflections

θ = 2.10–26.46°

μ = 1.725 mm⁻¹

T = 153(2) K

Rod

0.69 × 0.17 × 0.11 mm

Colourless

Data collection

Siemens SMART CCD diffractometer

2338 reflections with *I* > 2σ(*I*)

Exposures over 0.3° φ or ω rotation scans

Absorption correction:

multi-scan (SADABS;

Sheldrick, 1996)

T_{min} = 0.645, *T_{max}* = 0.827

6563 measured reflections

2490 independent reflections

R_{int} = 0.030

θ_{max} = 26.46°

h = -9 → 9

k = -11 → 11

l = -12 → 12

No standard reflections

intensity decay: none

Refinement

Refinement on *F*²

R[*F*² > 2σ(*F*²)] = 0.022

wR(*F*²) = 0.056

S = 1.061

2490 reflections

181 parameters

H atoms not refined

w = 1/[σ²(*F_o*²) + (0.0305*P*)²]

where *P* = (*F_o*² + 2*F_c*²)/3

(Δ/σ)_{max} = 0.001

Δρ_{max} = 0.585 e Å⁻³

Δρ_{min} = -0.613 e Å⁻³

Extinction correction: none

Scattering factors from

International Tables for Crystallography (Vol. C)

Table 1. Selected geometric parameters (Å, °)

Ag1—N1	2.371(2)	C4—C5	1.375(4)
Ag1—N1'	2.345(2)	C5—C6	1.379(3)
Ag1—S1'	2.4796(6)	S1—C2'	1.795(2)
Ag1—O11	2.560(2)	N1'—C2'	1.337(3)
N1—C2	1.339(3)	N1'—C6'	1.343(3)
N1—C6	1.344(3)	C2'—C3'	1.379(3)
C2—C3	1.381(3)	C3'—C4'	1.385(3)
C2—S1	1.793(2)	C4'—C5'	1.387(4)
C3—C4	1.390(4)	C5'—C6'	1.378(4)
N1'—Ag1—N1	83.59(6)	N1—C6—C5	123.1(2)
N1'—Ag1—S1'	135.08(5)	C2—S1—C2'	99.13(10)
N1—Ag1—S1'	130.82(5)	C2—S1—Ag1'	108.32(8)
N1'—Ag1—O11	83.17(6)	C2'—S1—Ag1'	106.94(7)
N1—Ag1—O11	98.28(6)	C2'—N1'—C6'	117.6(2)
S1'—Ag1—O11	112.94(4)	C2'—N1'—Ag1	119.53(15)
C2—N1—C6	116.8(2)	C6'—N1'—Ag1	122.9(2)
C2—N1—Ag1	118.06(15)	N1'—C2'—C3'	123.7(2)
C6—N1—Ag1	123.4(2)	N1'—C2'—S1	117.7(2)
N1—C2—C3	123.9(2)	C3'—C2'—S1	118.6(2)
N1—C2—S1	117.5(2)	C2'—C3'—C4'	117.9(2)
C3—C2—S1	118.6(2)	C3'—C4'—C5'	119.3(2)
C2—C3—C4	118.2(2)	C6'—C5'—C4'	118.6(2)
C5—C4—C3	118.6(2)	N1'—C6'—C5'	122.8(2)
C4—C5—C6	119.3(2)	N10—O11—Ag1	99.40(14)

Symmetry code: (i) 1 - *x*, -*y*, 2 - *z*.

Crystal decay was monitored by measurement of duplicate reflections. H atoms were placed at calculated positions. One ethanol solvate molecule per unit cell is disordered over two positions about a centre of symmetry (-*x*, 1 - *y*, 1 - *z*) located at the mid-point of the C—C bond.

Data collection: SMART (Siemens 1995). Cell refinement: SAINT (Siemens 1995). Data reduction: SAINT. Program(s) used to solve structure: SHELXS86 (Sheldrick, 1990). Program(s) used to refine structure: SHELXL93 (Sheldrick, 1993). Molecular graphics: SHELXL93. Software used to prepare material for publication: SHELXL93.

Supplementary data for this paper are available from the IUCr electronic archives (Reference: TA1195). Services for accessing these data are described at the back of the journal.

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A Dinuclear Tungsten(III) Complex Containing a Tungsten–Tungsten Triple Bond with an Asymmetric Arrangement of Ligands: $[\text{W}_2\text{Cl}_3(\text{OCMe}_3)_3(\text{HNMe}_2)_2]$

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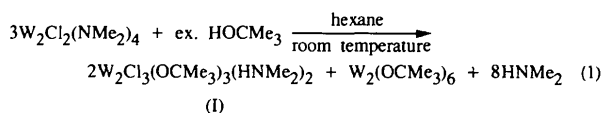
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Abstract

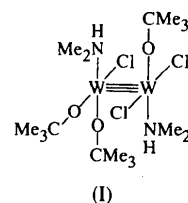
The title complex, tri-*tert*-butoxy- $1\kappa^2\text{O}, 2\kappa\text{O}$ -trichloro- $1\kappa\text{Cl}, 2\kappa^2\text{Cl}$ -bis(*N,N*-dimethylamine)- $1\kappa\text{N}, 2\kappa\text{N}$ -ditungsten(*W–W*), $[\text{W}_2\text{Cl}_3(\text{C}_4\text{H}_9\text{O})_3(\text{C}_2\text{H}_7\text{N})_2]$, adopts a dinuclear structure in which two tungsten(III) atoms are united by a $\text{W}\equiv\text{W}$ bond unsupported by bridging ligands. Both W atoms are coordinated to four ligand atoms that lie in a roughly square-planar arrangement. The two W atoms have different coordination environments: one is ligated by two *cis*-OR groups, one Cl and one HNMe_2 ligand, while the other is ligated by two *trans*-Cl ligands, one OR group and one HNMe_2 ligand.

Comment

There is now an extensive chemistry of ditungsten hexaalkoxides as templates for organometallic chemistry and catalysis (Chisholm, 1996). The $\text{W}_2(\text{OR})_6$ compounds are members of the well known family of so-called d^3 – d^3 ethane-like dimers (Chisholm, 1990), and they are readily prepared from $[\text{W}_2(\text{NMe}_2)_6]$ by an alcoholysis reaction (Akiyama *et al.*, 1979). Our attempt at the alcoholysis of $[\text{W}_2\text{Cl}_2(\text{NMe}_2)_4]$ by *tert*-butyl alcohol resulted in an unusual complex, $[\text{W}_2\text{Cl}_3(\text{OCMe}_3)_3(\text{HNMe}_2)_2]$, (I), by a possible disproportionation reaction as shown in equation (1),



since the $[\text{W}_2\text{Cl}_2(\text{NMe}_2)_4]$ compound is labile towards Cl for an NMe_2 exchange reaction (Akiyama *et al.*, 1977).



The title complex, (I), adopts a dinuclear structure in which two W^{III} atoms are united by a $\text{W}\equiv\text{W}$ bond unsupported by bridging ligands. The W–W distance, 2.3155 (5) Å, differs little from that observed in $[\text{W}_2\text{Cl}_2(\text{NMe}_2)_4]$, 2.301 (1) Å, and the subtle lengthening probably reflects steric interactions across the dinuclear center. Both W atoms are coordinated to four ligand atoms that lie in a roughly square-planar arrangement. The largest deviation of W–W–L angles from 90° for atoms W1 and W2 are O7–W1–W2 $108.9(2)^\circ$ and W1–W2–Cl17 $106.43(6)^\circ$, which reflect steric repulsive interactions across the $\text{W}\equiv\text{W}$ bond. The central $\text{W}_2\text{Cl}_3\text{O}_3\text{N}_2$ moiety adopts an eclipsed conformation. The two W atoms have different coordination environments: one is ligated by two *cis*-OR groups, one Cl and one HNMe_2 ligand, while the other is ligated by two *trans*-Cl ligands, one OR group and one HNMe_2 ligand. The disposition of two *trans*-Cl ligands in this complex is different from that in $[\text{W}_2\text{Cl}_3(\text{NMe}_2)_3(\text{PMe}_2\text{Ph})_2]$, in which the pair of Cl atoms coordinates one of the tungsten centers in a *cis* configuration (Ahmed *et al.*, 1985*a,b*). The W–O [1.885 (6), 1.911 (6) and 1.903 (6) Å] and W–Cl distances [2.390 (2), 2.358 (2), 2.363 (2) Å] are comparable with those in the $\text{W}_2(\text{OR})_6$ compounds and $[\text{W}_2\text{Cl}_2(\text{NMe}_2)_4]$. However, the W–N distances [2.255 (7) and 2.278 (8) Å] are notably longer than those in $[\text{W}_2(\text{NMe}_2)_6]$ and $[\text{W}_2\text{Cl}_2(\text{NMe}_2)_4]$, indicating that only single W–N bonds are formed, due to the protonation of NMe_2 to HNMe_2 .