

Table 1. Fractional atomic coordinates and equivalent isotropic displacement parameters (Å²)
$$U_{eq} = (1/3) \sum_i \sum_j U^{ij} a^i a^j$$

| | x | y | z | U _{eq} |
|------|--------------|---------------|-------------|-----------------|
| Er | 1/2 | 0.521683 (15) | 3/4 | 0.01841 (6) |
| O1 | 0.56702 (9) | 0.46522 (18) | 0.9647 (2) | 0.0359 (5) |
| O2 | 0.46523 (9) | 0.34097 (17) | 0.8086 (2) | 0.0303 (4) |
| O3 | 0.58625 (8) | 0.42206 (19) | 1.1975 (2) | 0.0306 (4) |
| O4 | 0.53501 (9) | 0.68217 (17) | 0.9027 (2) | 0.0294 (4) |
| N1 | 0.83637 (17) | 0.2443 (5) | 1.4600 (5) | 0.0979 (17) |
| N2† | 0.3868 (4) | -0.1176 (8) | 0.9039 (11) | 0.092 (3) |
| C1 | 0.60188 (11) | 0.4326 (2) | 1.0835 (3) | 0.0234 (5) |
| C2 | 0.66728 (12) | 0.4057 (2) | 1.0934 (3) | 0.0279 (6) |
| C3 | 0.70490 (13) | 0.3566 (3) | 1.2181 (3) | 0.0332 (7) |
| C4 | 0.76599 (14) | 0.3358 (3) | 1.2287 (4) | 0.0459 (9) |
| C5 | 0.80512 (16) | 0.2841 (4) | 1.3580 (5) | 0.0655 (13) |
| C6 | 0.78943 (16) | 0.3633 (4) | 1.1153 (5) | 0.0583 (11) |
| C7 | 0.75127 (17) | 0.4116 (4) | 0.9902 (5) | 0.0610 (13) |
| C8 | 0.69056 (15) | 0.4332 (4) | 0.9791 (4) | 0.0460 (8) |
| C9 | 1/2 | 0.2893 (3) | 3/4 | 0.0279 (8) |
| C10 | 1/2 | 0.1651 (4) | 3/4 | 0.0315 (9) |
| C11 | 0.46048 (16) | 0.1079 (3) | 0.8081 (4) | 0.0397 (7) |
| C12 | 0.4600 (2) | -0.0074 (3) | 0.8063 (5) | 0.0499 (9) |
| C13† | 0.4211 (4) | -0.0680 (7) | 0.8592 (9) | 0.0556 (19) |
| C14 | 1/2 | -0.0653 (5) | 3/4 | 0.0563 (14) |

† Site occupancy = 0.50.

Table 2. Selected bond lengths (Å)

| | | | |
|--------------------|-------------|---------|------------|
| Er—O1 | 2.2712 (19) | O3—C1 | 1.253 (3) |
| Er—O3 [†] | 2.2764 (18) | N1—C5 | 1.131 (5) |
| Er—O4 | 2.412 (2) | N2—C13 | 1.164 (10) |
| Er—O2 | 2.439 (2) | C1—C2 | 1.503 (3) |
| O1—C1 | 1.243 (3) | C9—C10 | 1.496 (6) |
| O2—C9 | 1.265 (3) | C12—C13 | 1.359 (9) |

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

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

| D—H...A | D—H | H...A | D...A | D—H...A |
|--------------------------|------------|----------|-----------|---------|
| O4—H8...N1 ⁱ | 0.918 (18) | 2.09 (3) | 2.935 (4) | 153 (3) |
| O4—H7...O2 ⁱⁱ | 0.901 (18) | 1.92 (2) | 2.782 (3) | 160 (4) |

Symmetry codes: (i) 3/2 - x, 1/2 + y, 5/2 - z; (ii) 1 - x, 1 - y, 2 - z.

All H atoms were located by difference Fourier synthesis. The water H atoms were refined with a rigid model and the other H atoms were refined isotropically.

Data collection: *CAD-4 ARGUS Software* (Nonius, 1996). Cell refinement: *CAD-4 ARGUS Software*. Data reduction: *MoLEN* (Fair, 1990). Program(s) used to solve structure: *SHELXS97* (Sheldrick, 1990). Program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997). Molecular graphics: *XPMA* and *ZORTEP* (Zsolnai, 1998). Software used to prepare material for publication: *SHELXL97*.

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: DA1072). Services for accessing these data are described at the back of the journal.

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Bis(4,4'-disulfanediyl)pyridinium di-μ-chloro-bis[dichlorocuprate(II)] bis(tetra-fluoroborate)

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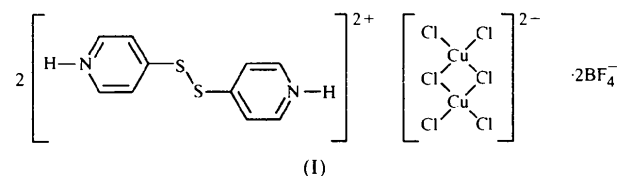
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Abstract

In the title compound, (C₁₀H₁₀N₂S₂)₂[Cu₂Cl₆](BF₄)₂, the [Cu₂Cl₆]²⁻ anions associate through weak Cu...Cl contacts to form polymeric [CuCl₃]_nⁿ⁻ chains. Hydrogen bonding between the chloride anions of these chains and the pyridinium protons, and between the pyridinium protons and the BF₄⁻ anions, results in the formation of weakly associated ribbons.

Comment

The title compound, (I), isolated during our studies into the formation of extended structures by copper halide complexes and bridging bipyridyl ligands, exists as an air-stable red solid.



1.91 Å is also short, and this distance and the nearly linear N—H...F angle of 170° characterize it as a close N—H...F hydrogen-bonding interaction.

The bis(4-pyridinium)disulfide cation is twisted with a C—S—S—C torsion angle of -81.5(2)°, which is comparable to the value of 86.6° reported for the only structurally characterized example of the bis(4-pyridyl)disulfide ligand, namely the bis(triiodide) salt of *trans*-[μ-bis(4-pyridyl)disulfide]bis[bis{o-(Me₂As)₂-C₆H₄}ClRu]²⁺ (Coe *et al.*, 1997). This bent arrangement results in the BF₄⁻/bipyridinium/[Cu₂Cl₆]²⁻/bipyridinium/BF₄⁻ units undulating across the plane of the hydrogen-bonded ribbon (Fig. 2).

Experimental

Crystals of the title compound were prepared by layering a solution of Cu(BF₄)₂ (0.02 g, 0.06 mmol) in MeCN (10 ml) over a solution of bis(4-pyridyl) disulfide (0.025 g, 0.20 mmol) in CH₂Cl₂ (10 ml). Red acicular crystals appeared over a period of several weeks. IR spectroscopy confirmed the presence of BF₄⁻ anions.

Crystal data

| | |
|--|--|
| (C ₁₀ H ₁₀ N ₂ S ₂) ₂ [Cu ₂ Cl ₆]- (BF ₄) ₂ | Mo Kα radiation |
| <i>M_r</i> = 958.04 | λ = 0.71073 Å |
| Triclinic | Cell parameters from 40 reflections |
| <i>P</i> $\bar{1}$ | θ = 20–35° |
| <i>a</i> = 5.9096 (11) Å | <i>μ</i> = 2.081 mm ⁻¹ |
| <i>b</i> = 9.9845 (17) Å | <i>T</i> = 150 (2) K |
| <i>c</i> = 14.394 (3) Å | Needle |
| α = 95.053 (17)° | 0.70 × 0.10 × 0.06 mm |
| β = 93.762 (19)° | Dark red |
| γ = 99.544 (17)° | |
| <i>V</i> = 831.5 (3) Å ³ | |
| <i>Z</i> = 1 | |
| <i>D_x</i> = 1.913 Mg m ⁻³ | |
| <i>D_m</i> not measured | |

Data collection

| | |
|---|---|
| Stoe Stadi-4 four-circle diffractometer | 2335 reflections with <i>I</i> > 2σ(<i>I</i>) |
| ω/2θ scans | <i>R</i> _{int} = 0.067 |
| Absorption correction: numerical (<i>XRED</i> ; Stoe & Cie, 1997a) | θ _{max} = 25.03° |
| <i>T</i> _{min} = 0.906, <i>T</i> _{max} = 0.945 | <i>h</i> = -7 → 7 |
| 3244 measured reflections | <i>k</i> = -11 → 11 |
| 2911 independent reflections | <i>l</i> = -13 → 17 |
| | 3 standard reflections frequency: 60 min intensity variation: ±4.2% |

Refinement

| | |
|---|---|
| Refinement on <i>F</i> ² | (Δ/σ) _{max} = 0.001 |
| <i>R</i> [<i>F</i> ² > 2σ(<i>F</i> ²)] = 0.045 | Δρ _{max} = 0.55 e Å ⁻³ |
| <i>wR</i> (<i>F</i> ²) = 0.082 | Δρ _{min} = -0.43 e Å ⁻³ |
| <i>S</i> = 1.18 | Extinction correction: none |

2911 reflections

208 parameters

H atoms constrained

$$w = 1/[\sigma^2(F_o^2) + 2.647P]$$

$$\text{where } P = (F_o^2 + 2F_c^2)/3$$

Scattering factors from

*International Tables for
Crystallography* (Vol. C)

Table 1. Selected geometric parameters (Å, °)

| | | | |
|---------------------------|-------------|----------------------------|-------------|
| Cu1—C11 | 2.2510 (13) | Cu1—C13 | 2.2609 (14) |
| Cu1—C12 | 2.3433 (14) | Cu1—C13 ⁱⁱ | 2.6643 (14) |
| Cu1—C12' | 2.2820 (14) | | |
| C11—Cu1—C12' | 92.67 (5) | C12—Cu1—C13 | 88.15 (5) |
| C11—Cu1—C12 | 160.92 (5) | C12'—Cu1—C13 ⁱⁱ | 92.46 (5) |
| C11—Cu1—C13 | 92.88 (5) | C12—Cu1—C13 ⁱⁱ | 95.82 (5) |
| C11—Cu1—C13 ⁱⁱ | 103.13 (5) | C13—Cu1—C13 ⁱⁱ | 93.27 (5) |
| C12'—Cu1—C12 | 84.27 (5) | Cu1 ⁱ —C12—Cu1 | 95.73 (5) |
| C12'—Cu1—C13 | 170.92 (5) | Cu1—C13—Cu1 ⁱⁱ | 86.73 (5) |
| C4—S1—S2—C7 | -81.5 (2) | | |

Symmetry codes: (i) -x, -y, -z; (ii) 1 - x, -y, -z.

Table 2. Hydrogen-bonding geometry (Å, °)

| <i>D</i> —H... <i>A</i> | <i>D</i> —H | H... <i>A</i> | <i>D</i> ... <i>A</i> | <i>D</i> —H... <i>A</i> |
|-------------------------|-------------|---------------|-----------------------|-------------------------|
| N10—H10A...C11 | 0.88 | 2.49 | 3.237 (4) | 143 |
| N10—H10A...C13 | 0.88 | 2.49 | 3.148 (4) | 132 |
| N1—H1A...F1 | 0.88 | 1.91 | 2.781 (6) | 170 |

The crystal was cooled using an Oxford Cryosystems open-flow cryostat operating at 150 K (Cosier & Glazer, 1986). H1A and H10A were found from Δ*F* syntheses and subsequently restrained to lie at a distance of 0.88 Å from their parent N atoms, N1 and N10, respectively. All other H atoms were included at geometrically calculated positions; each was constrained to ride at a distance of 0.95 Å from its parent C atom. For all H atoms, displacement parameters were constrained such that *U*_{iso}(H) = 1.2*U*_{eq}(C).

Data collection: *STADIA* (Stoe & Cie, 1997b). Cell refinement: *STADIA*. Data reduction: *XRED* (Stoe & Cie, 1997a). Program(s) used to solve structure: *SHELXS97* (Sheldrick, 1990). Program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997). Molecular graphics: *SHELXTL/PC* (Sheldrick, 1994). Software used to prepare material for publication: *SHELXL97*.

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: GD1036). Services for accessing these data are described at the back of the journal.

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(1,4-Dioxane-O){3,3',5,5'-tetrachloro-2,2'-[4-methyl-4-azaheptane-1,7-diyl-bis(nitrilomethylidene-N)]diphenolato-O,O'}nickel(II), [Ni(3,5-Cl₄salMetrien)]

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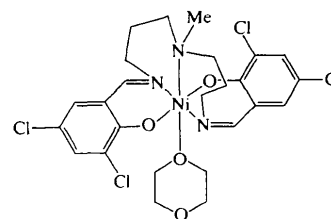
Abstract

In the title compound, [Ni(C₂₁H₂₁Cl₄N₃O₂)(C₄H₈O₂)], the Ni atom has a distorted octahedral coordination geometry in which the pentadentate Schiff base ligand acts as an N₃O₂ donor and a molecule of 1,4-dioxane occupies the remaining coordination position. The N atoms adopt a meridional arrangement, coplanar with the O-donor atom of the dioxane molecule, and the ligand O atoms are *trans*-related. This conformation results in an approximate square-pyramidal coordination for the pentadentate ligand, with the dioxane molecule *trans* to the amine N atom.

Comment

We are currently interested in the redox properties of nickel(II) complexes with mixed-donor polydentate Schiff base ligands (Freire & de Castro, 1998; Azevedo *et al.*, 1994; Carrondo *et al.*, 1993; de Castro & Freire, 1990) due to their potential use as synthetic catalysts and as models for metalloenzymes. We reported previously that nickel(II) complexes with N₂O₂-tetradentate Schiff base ligands derived from salicylaldehyde and diamines are oxidized to nickel(III) only in the presence of strong donating solvents (Freire & de Castro, 1998; Vilas-Boas *et al.*, 1997; Azevedo *et al.*, 1994; Carrondo *et al.*, 1993; de Castro & Freire, 1990). In order to

overcome the strong solvent effect on the oxidative properties of the latter complexes, we have prepared a group of pentadentate Schiff base ligands using the same aldehyde derivatives but condensed with triamines, and have studied the feasibility of their nickel(II) complexes being oxidized to nickel(III). Due to the variability of coordination modes of these pentadentate ligands (Freyberg *et al.*, 1979; Healey *et al.*, 1975), we found it necessary to determine the structure of the title complex, [Ni(3,5-Cl₄salMetrien)], to ascertain the coordination mode of the Schiff base ligand.



[Ni(3,5-Cl₄salMetrien)]

The structure consists of discrete molecules in which the Ni atom has a distorted octahedral coordination geometry, with the pentadentate ligand acting as an N₃O₂ donor and a molecule of 1,4-dioxane occupying the remaining coordination site (Fig. 1). The N atoms adopt a *mer* arrangement, coplanar with the O-donor atom of the dioxane molecule, and consequently the Schiff base ligand O atoms are *trans*-related. In the observed conformation, the pentadentate ligand coordination is approximately square pyramidal, leaving the other axial position *trans* to the amine N atom free to bind a dioxane molecule. The equatorial bond distances are similar, but the Ni—N(amine) axial bond distance is much longer than any of the equatorial ones. All bond distances are longer than those observed in the homologous complexes with the Schiff base ligand derived from the non-substituted aldehyde, which exhibit a distorted trigonal-bipyramidal structure (Di Vaira *et al.*, 1971). The longest bond is that of Ni—O(dioxane), as expected for a weakly coordinated monodentate ligand. The angular distortion from normal octahedral geometry is in the range 3–11°, and the maximum deviation of the Ni atom from the least-squares equatorial plane of coordination (N1A/O1A/N1/O1) is 0.093 (1) Å. However, the ligand chelate-ring atoms (N1A/C7A/C6A/C1A/O1A and N1/C7/C6/C1/O1) define planes that make angles of 34.2 (1) and 31.6 (1)°, respectively, with the plane of coordination, and each is almost coplanar with the plane defined by the atoms of the corresponding benzene ring; the angle between the two salicyl moieties is 71.2 (1)°. The umbrella shape of the molecule may be a consequence of steric constraints imposed by the long flexible —(CH₂)₃—N(CH₃)—(CH₂)₃— imine bridge, which exhibits disorder in some of the C atoms; this dis-