

The Cu ion is coordinated to the four N atoms of the macrocycle and a Cl⁻ ion to form a distorted square-pyramidal geometry. The cation possesses crystallographic twofold symmetry through the Cu—Cl bond. Both 1,3-diazacyclopentane ring moieties in [Cu(L)Cl]ClO₄ are situated in the same direction with respect to the coordination plane toward the apical Cl⁻ ligand while they are situated oppositely in square-planar [Ni(L)]Cl₂. The Cu and Ni complexes correspond to the *trans*-I and *trans*-III conformers, respectively (Thöm, Fox, Boeyens & Hancock, 1984).

Two pairs of the twofold-related N donors are disposed [$\pm 0.129(8) \text{ \AA}$] on the opposite sides of their least-squares plane, showing a slight tetrahedral distortion. The Cu ion lies $0.316(1) \text{ \AA}$ above this plane toward the Cl⁻ ion. The five-membered chelate ring assumes a half-chair form [N—C—C—N $58(1)^\circ$]. The six-membered chelate ring assumes a conformation intermediate between the normal and half-chair forms. The 1,3-diazacyclopentane ring moiety assumes an envelope form [N—C—C—N $8.4(9)^\circ$] and is situated perpendicular to the basal coordination plane with a dihedral angle of $102(1)^\circ$.

Cu—N(6)(tertiary) [$2.043(8) \text{ \AA}$] is slightly longer than Cu—N(3)(secondary) [$2.022(8) \text{ \AA}$]. These coordination bond distances are consistent with those of Cu complexes of the 14-membered macrocycle (Lee, Lee, Juang & Chung, 1985) and longer than those of [Ni(L)]Cl₂. The Cu—Cl bond distance, $2.483(4) \text{ \AA}$, is the typical value for Cu^{II} complexes. The average C—N distance involving coordinated tertiary N(6) ($1.49 \pm 0.02 \text{ \AA}$) is slightly shorter than

that involving coordinated secondary N(3) ($1.53 \pm 0.02 \text{ \AA}$). The Cl⁻ ligand makes a close contact with C(7) [$3.348(15) \text{ \AA}$] which is shorter than the van der Waals contact of 3.5 \AA (Bondi, 1964).

Crystal packing is shown in Fig. 2. The perchlorate anion is located on the twofold symmetry axis and statistically disordered in two positions with almost equal site occupancy. One O atom of the perchlorate ion may be involved in a hydrogen bond [N(3)⋯O(2), $3.09(2)$, N(3)—H, $0.90(2)$, H⋯O(2), $2.24(3) \text{ \AA}$, N(3)—H⋯O(2), $159(3)^\circ$] although disordering phenomena may diminish this effect. The Cl⁻ ligand is $4.087(2) \text{ \AA}$ above the Cu ion of the cation related by one unit-cell translation along the *c* axis.

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Structure of *trans*-Dichlorotetrakis(dimethyl sulfoxide)rhodium(III) Tetrafluoroborate

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Abstract. (OC-6-13)-Dichlorobis(dimethyl sulfoxide-O)bis(dimethyl sulfoxide-S)rhodium(III) tetrafluoroborate, [RhCl₂(C₂H₆OS)₄]BF₄, $M_r = 573.15$, triclinic, $P\bar{1}$, $a = 9.178(4)$, $b = 10.459(3)$, $c = 11.194(5) \text{ \AA}$, $\alpha = 92.71(2)$, $\beta = 96.77(2)$, $\gamma = 91.43(2)^\circ$, $V = 1065.4(7) \text{ \AA}^3$, $Z = 2$, $D_x = 1.787 \text{ g cm}^{-3}$, $\lambda(\text{Mo } K\alpha) = 0.7107 \text{ \AA}$, $\mu(\text{Mo } K\alpha) = 14.6 \text{ cm}^{-1}$, $F(000) = 576$, $T = 294 \text{ K}$, $R = 0.032$, wR

$= 0.042$ for 4017 unique observed reflections. The structure of the cation is characterized by a *trans*-Cl octahedral coordination around the metal atom. Two of the four dimethyl sulfoxide (dmsO) ligands are O-bonded to the Rh atom, the others are S-bonded, with O—dmsO *trans* to S—dmsO. Average bond distances are: Rh—Cl, $2.327(4)$; Rh—S, $2.259(7)$; Rh—O, $2.0798(8) \text{ \AA}$.

Table 1. Final fractional coordinates and equivalent isotropic thermal parameters (Å²) with their *e.s.d.*'s
$$B_{eq} = (4/3)[a^2B(1,1) + b^2B(2,2) + c^2B(3,3) + ab(\cos\gamma)B(1,2) + ac(\cos\beta)B(1,3) + bc(\cos\alpha)B(2,3)].$$

	<i>x</i>	<i>y</i>	<i>z</i>	<i>B</i> _{eq}
Rh	0.06482 (3)	0.28475 (2)	0.28097 (2)	2.541 (4)
C11	0.0816 (1)	0.3406 (1)	0.08446 (8)	4.33 (2)
C12	0.0462 (1)	0.24400 (9)	0.48146 (7)	4.00 (2)
S1	-0.0301 (1)	0.08847 (9)	0.21965 (9)	3.78 (2)
S2	0.30172 (9)	0.22592 (8)	0.30598 (8)	3.36 (2)
S3	0.23184 (9)	0.55732 (8)	0.28218 (7)	3.12 (1)
S4	-0.1886 (1)	0.47480 (9)	0.22195 (9)	3.81 (2)
F1	-0.5378 (4)	0.6984 (4)	0.1534 (4)	9.0 (1)
F2	-0.4724 (5)	0.8675 (4)	0.2731 (3)	9.1 (1)
F3	-0.3304 (4)	0.7953 (5)	0.1388 (4)	10.4 (1)
F4	-0.5283 (9)	0.8873 (5)	0.0802 (5)	20.3 (2)
O1	0.0755 (4)	-0.0118 (3)	0.2051 (4)	6.31 (8)
O2	0.4030 (3)	0.3314 (3)	0.3525 (3)	5.17 (7)
O3	0.1237 (3)	0.4720 (2)	0.3421 (2)	3.20 (4)
O4	-0.1528 (3)	0.3388 (2)	0.2637 (3)	4.07 (5)
C11	-0.1488 (6)	0.0931 (5)	0.0837 (4)	5.8 (1)
C12	-0.1554 (6)	0.0362 (5)	0.3176 (5)	6.5 (1)
C21	0.3333 (5)	0.0971 (4)	0.4027 (4)	5.21 (9)
C22	0.3586 (6)	0.1598 (5)	0.1709 (4)	5.6 (1)
C31	0.1238 (5)	0.6834 (4)	0.2231 (4)	4.44 (8)
C32	0.3280 (5)	0.6443 (4)	0.4089 (4)	4.54 (8)
C41	-0.3311 (6)	0.4473 (5)	0.1023 (4)	6.1 (1)
C42	-0.2907 (6)	0.5363 (4)	0.3349 (4)	5.2 (1)
B	-0.4718 (6)	0.8167 (5)	0.1597 (5)	4.8 (1)

Table 2. Bond distances (Å) and angles (°)

Rh—C11	2.3238 (9)	S2—C22	1.773 (5)
Rh—C12	2.3293 (9)	S3—O3	1.550 (3)
Rh—S1	2.2539 (9)	S3—C31	1.776 (4)
Rh—S2	2.2638 (9)	S3—C32	1.778 (4)
Rh—O3	2.080 (2)	S4—O4	1.549 (3)
Rh—O4	2.079 (3)	S4—C41	1.766 (5)
S1—O1	1.462 (4)	S4—C42	1.767 (5)
S1—C11	1.768 (5)	F1—B	1.359 (6)
S1—C12	1.774 (6)	F2—B	1.353 (6)
S2—O2	1.461 (3)	F3—B	1.368 (7)
S2—C21	1.776 (5)	F4—B	1.256 (8)
C11—Rh—S1	92.29 (4)	Rh—S2—C21	113.5 (2)
C11—Rh—S2	91.99 (4)	Rh—S2—C22	112.2 (2)
C11—Rh—O3	89.79 (7)	O2—S2—C21	107.7 (2)
C11—Rh—O4	89.73 (9)	O2—S2—C22	108.8 (2)
C12—Rh—S1	91.24 (4)	C21—S2—C22	101.1 (2)
C12—Rh—S2	89.56 (3)	O3—S3—C31	104.6 (2)
C12—Rh—O3	86.46 (7)	O3—S3—C32	101.9 (2)
C12—Rh—O4	88.70 (9)	C31—S3—C32	98.1 (2)
S1—Rh—S2	95.77 (3)	O4—S4—C41	103.8 (2)
S1—Rh—O4	84.61 (7)	O4—S4—C42	102.6 (2)
S2—Rh—O3	91.66 (7)	C41—S4—C42	99.8 (2)
O3—Rh—O4	87.89 (9)	Rh—O3—S3	123.1 (1)
Rh—S1—O1	116.3 (1)	Rh—O4—S4	118.4 (2)
Rh—S1—C11	111.3 (2)	F1—B—F2	108.0 (5)
Rh—S1—C12	110.6 (2)	F1—B—F3	104.8 (4)
O1—S1—C11	108.3 (2)	F1—B—F4	112.7 (5)
O1—S1—C12	108.8 (2)	F2—B—F3	109.4 (4)
C11—S1—C12	100.3 (2)	F2—B—F4	113.3 (5)
Rh—S2—O2	112.8 (1)	F3—B—F4	108.2 (6)

Introduction. In the course of a general study on halide-dimethyl sulfoxide (dmsO) hexacoordinated ruthenium and rhodium complexes, acting as possible antitumor agents (Mestroni *et al.*, 1989), [RhCl₂(dmsO)₄][BF₄] was synthesized by treating [RhCl₂(dmsO)₃] (James & Morris, 1980) with the stoichiometric amount of AgBF₄ in a refluxing acetone/dimethyl sulfoxide (80:1) solution. Dissolution of the crude product in warm acetone and addition of small amounts of diethyl ether yielded crystals suitable for X-ray analysis.

The structure of the title compound could not be unambiguously obtained from NMR evidence (Barnes, Goggin & Goodfellow, 1979).

Experimental. Crystal dimensions approximately 0.7 × 0.4 × 0.6 mm. Weissenberg and precession photographs indicated crystals to be triclinic. Nonius CAD-4 diffractometer, graphite-monochromated Mo Kα radiation. Lattice parameters refined by least-squares fit of 25 reflections in the range 15 < θ < 21°. Intensity data measured by the ω/2θ scan technique, ω-scan angle = (1.05 + 0.35tanθ)°; scan rate 8–24° min⁻¹, max. 2θ = 54°. Three standard reflections (284, 630, 373), monitored every 4000 s, showed no decay. Orientation matrix checked every 800 reflections. 5046 reflections collected (3 ≤ θ ≤ 27°; -11 ≤ h ≤ 11, -13 ≤ k ≤ 13, 0 ≤ l ≤ 14), 4017 judged significant [I ≥ 3.0σ(I)]. σ(F_o) based on counting statistics; empirical absorption correction applied using ψ scans of four reflections at θ > 15° (correction factors in the range 0.915–1.000, average

transmission factor 0.968); Lorentz and polarization corrections. Structure solved by the heavy-atom method. H atoms located on the basis of ideal bond lengths (C—H, 0.95 Å) and angles and not included in the least-squares refinement. Refinement using full-matrix least-squares method with anisotropic thermal factors for non-H atoms led to *R* = 0.032, *wR* = 0.042, *S* = 0.80, (Δ/σ)_{max} = 0.02. Function minimized ∑_{hkl}w_{hkl}(|F_o| - |F_c|)², w = 1/[1 + σ²(F_o) + (0.025F_o)²]. Max. residual Δρ 0.77 e Å⁻³, around F4. The extinction parameter (*g*; Stout & Jensen, 1968) is 1.7 (4) × 10⁻⁷. Atomic scattering factors, anomalous-dispersion terms and programs as in the Enraf-Nonius SDP (B. A. Frenz & Associates, Inc., 1985). All computations carried out on a MicroVAX 2000.

Discussion. Final fractional coordinates and equivalent isotropic thermal parameters of non-H atoms are given in Table 1 and bond lengths and angles in Table 2.* The structure of the cation is shown in Fig. 1. The difference Fourier maps and the isotropic thermal factors showed that the F atoms, especially F4, were disordered. Different disorder models of the BF₄ anion did not refine satisfactorily. Eventually,

* Lists of structure factors, anisotropic thermal parameters and H-atom parameters have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 53621 (20 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

the F atoms were located in an average position and refined anisotropically, allowing them to assume high thermal factors. The other structural parameters were not affected by the different disorder models.

The title cation has a distorted octahedral coordination around the Rh atom with two Cl atoms in *trans* positions. Two of the four dmsO ligands are O-bonded in a *cis* arrangement, while the other two *cis*-coordinated dmsO's are S-bonded. In agreement with the complex structure, the solid-state infrared spectrum shows four bands in the S=O stretching region, two for the S-bonded (1148 and 1135 cm^{-1}) and two for the O-bonded (916 and 905 cm^{-1}) dmsO's (Barnes *et al.*, 1979). The corresponding Rh—O and Rh—S stretching bands fall at 520, 497 and 440, 427 cm^{-1} , respectively (Fadeev, Kukushkin & Khokhryakov, 1975).

The average Rh—Cl bond length of 2.327 (4) Å is close to the values found in other *trans* Cl—Rh^{III}—Cl groups: 2.33 (2) Å in [RhCl₃(dmsO-S)(py)₂] (Colamarino & Orioli, 1976) and 2.34 (1) Å in [RhCl₃(dmsO-S)₂(dmsO-O)] (Sokol & Porai-Koshits, 1974). Similarly, the Rh—S, *trans* to dmsO-O, bond distances [av. 2.259 (7) Å] are comparable, within experimental error, to 2.231 (7) Å found in [RhCl₃(dmsO-S)₂(dmsO-O)] (Sokol & Porai-Koshits, 1974).

As already observed (Alessio, Mestroni, Nardin, Attia, Calligaris, Sava & Zorzet, 1988; Annibale, Cattalini, Bertolasi, Ferretti, Gilli & Tobe, 1989; Bancroft, Cotton & Verbruggen, 1989) in dmsO-S the S—O bond distance [av. 1.462 (1) Å] is markedly shorter than that of dmsO-O [av. 1.550 (1) Å] owing to the considerable decrease of the double-bond character of the S—O bond upon coordination *via* oxygen.

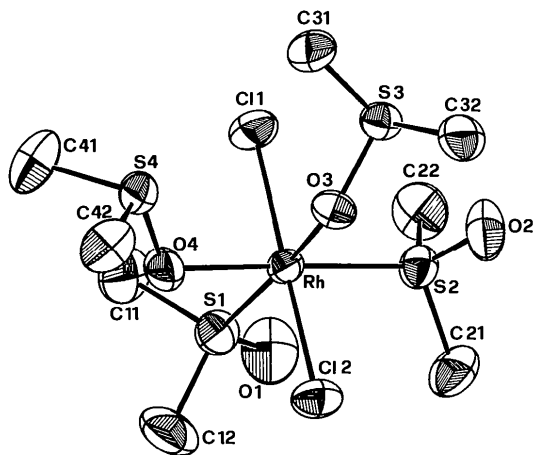


Fig. 1. ORTEP (Johnson, 1965) drawing and numbering scheme for non-H atoms of *trans*-[RhCl₂(dmsO)₄]⁺.

The compression action of the lone pair of the tetrahedral S atom on the bonding pairs in dmsO-O justifies the narrowing of the O—S—C bond angles passing from S-bonded [av. 108.3 (6)°] to O-bonded [av. 103 (1)°] dmsO. The narrowing of the C—S—C bond angles, from dmsO-S to dmsO-O, is much less marked, probably because of the steric hindrance of the methyl H atoms.

The ability of sulfoxides to coordinate *via* oxygen or *via* sulfur is determined by the interplay between electronic and steric effects. Recent available data (Alessio, Milani, Mestroni, Calligaris, Faleschini & Attia, 1990) indicate that in Ru^{II} complexes ruthenium prefers coordination *via* sulfur rather than *via* oxygen. This may be rationalized in terms of the HSAB (Hard Soft Acid Base) principle (Pearson, 1990). In fact, Ru^{II}, which may be considered a 'soft' acid, is expected to prefer coordination to a 'soft' base such as sulfur, rather than to a 'hard' base like oxygen. In any case, this type of bonding is controlled by the ligand steric hindrance and the π back-bonding competition between sulfur *trans* ligands. In fact, in *trans*-[RuCl₂(dmsO)₄] all the dmsO molecules are S-bonded but the complex is thermodynamically unstable because of the π back-bonding competition between *trans* sulfur ligands and steric interactions, arising from the overcrowding in the equatorial plane (Alessio *et al.*, 1988). On the contrary, the isoelectronic title complex, *trans*-[RhCl₂(dmsO)₄]⁺, is stable, having two dmsO's S-bonded and the other two O-bonded. The stability of this complex may be explained considering the 'borderline' acid character of Rh^{III} (Pearson, 1990), made 'harder' by the net positive charge of the metal complex, for which the S-bonding does not prevail over the O-bonding. Furthermore, the O-bonding reduces the steric strain energy and the π back-bonding competition between *trans* ligands, even if such an effect should be less pronounced than in the case of metals with lower oxidation states, because of the lower electron density on the metal center.

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New Precursors in the Chemistry of IVB Transition Metal Alkoxides. III. Synthesis and Structure of Zr₂Co₂(μ₃-OC₃H₇)₂(μ₂-OC₃H₇)₄(OC₃H₇)₄(acetylacetonate)₂

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Abstract. Bis(acetylacetonato)-bis(μ₃-propanolato)-1:2:4κO;2:3:4κO'-tetrakis(μ₂-propanolato)-1:2κO;-1:4-κO;2:3κO;3:4κO-tetrakis(propanolato)-2κ²O,-4κ²O-dicobaltdizirconium, Zr₂Co₂(OC₃H₇)₁₀(O₂C₅H₈)₂, *M_r* = 1091.43, monoclinic, *P*2₁/*n*, *a* = 12.753 (3), *b* = 16.500 (3), *c* = 13.485 (2) Å, β = 99.27 (2)°, *V* = 2800.6 Å³, *Z* = 2, *D_x* = 1.29 Mg m⁻³, λ(Mo *Kα*) = 0.71069 Å, μ = 4.88 mm⁻¹, *F*(000) = 1124, room temperature, *R* = 0.057 for 2798 independent [*I* > 3σ(*I*)] reflections. The centrosymmetric molecule is tetranuclear. The Zr atom has a very distorted octahedral environment and the Co atom a distorted trigonal bipyramidal surrounding. The alkoxy groups show three different coordination schemes.

Introduction. The hydrolysis of bimetallic alkoxides allows the synthesis of very homogeneous mixed metal oxides *via* the sol-gel process (Dislich, 1988). However, these starting products are frequently extremely unstable. Recent studies (Schmid, Mosset & Galy, 1990) from this laboratory show that they can be stabilized by a chelating ligand such as acetylacetonate (Hacac).

The reaction of zirconium *n*-propanolate on cobalt(II) acetylacetonate yields a new hexanuclear precursor: Zr₂Co₄(μ₆-O)(μ₂-OC₃H₇)₈(OC₃H₇)₂(acac)₄ (Schmid, Mosset & Galy, 1991). We report now the X-ray structure of the second product in this reaction: Zr₂Co₂(μ₃-OC₃H₇)₂(μ₂-OC₃H₇)₄(OC₃H₇)₄(acac)₂.

Experimental. 0.0082 mol of cobalt(II) acetylacetonate is suspended in 100 ml *n*-propanol, dried on

sodium and distilled under dry nitrogen. After the addition of 0.0328 mol of zirconium *n*-propanolate, the solution is stirred and refluxed for 24 h under nitrogen. This solution is then concentrated until one third of the solvent is removed and rapidly cooled in the refrigerator. Violet single crystals grow slowly; 0.25 × 0.35 × 0.15 mm; Enraf-Nonius CAD-4 diffractometer; graphite-monochromatized Mo *Kα* radiation; 25 reflections (8 < θ < 15°) for refined unit-cell parameters; θ/2θ scan mode; scan width 1.2°; independent reflections with 3 < θ < 19°; range of *hkl*: 0 < *h* < 11, 0 < *k* < 15, -12 < *l* < 12; no intensity deterioration of the three standard reflections; *Lp* corrections, no absorption correction; 2798 independent reflections with *I* > 3σ(*I*); metal positions from Patterson function, other non-H atoms from difference-Fourier syntheses; anisotropic full-matrix least-squares refinement on *F*; 262 refined parameters; unit weights; *R* = 0.057; *wR* = 0.055; (Δ/σ)_{max} = 0.1; final Δρ values < 0.6 e Å⁻³. Calculations performed with *SHELX76* (Sheldrick, 1976); scattering factors from *International Tables for X-ray Crystallography* (1974, Vol. IV, pp. 99–101, 149–150).

Discussion. Final atomic coordinates for the non-H atoms are listed in Table 1* and selected bond distances and angles in Table 2.

* Lists of structure factors and anisotropic thermal parameters have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 53643 (15 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.