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trans-(2-Acetylpyridine-κ^2*N*,*O*)-dichlorobis(dimethyl sulfoxide-κ*S*)-ruthenium(II)

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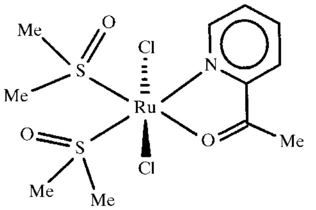
In the title complex, $[RuCl_2(C_7H_7NO)(C_2H_6OS)_2]$, the metal ion is at the centre of a distorted octahedral $NOCl_2S_2$ coordination sphere. The neutral 2-acetylpyridine ligand binds to the metal ion through the pyridine N and carbonyl O atoms, forming a five-membered chelate ring. The monodentate *S*-coordinating dimethyl sulfoxide molecules are mutually *cis*, and the two remaining positions in the coordination sphere are occupied by two mutually *trans* Cl^- ions.

Comment

Dimethyl sulfoxide (dmso) is an ambidentate ligand, in that it can bind a metal ion *via* the O or the S atom. Interest in complexes with this ligand is primarily directed towards gaining an understanding of the nature of the bond between the metal and the coordinating atom (Calligaris & Carugo, 1996; Sano & Taube, 1994). In general, coordination *via* O is preferred by harder high-valent metal ions, while *S*-coordination is favoured by softer low-valent metal ions. Although dmso-containing ruthenium complexes have been known for some time (Evans *et al.*, 1973), the recent discovery of anticancer activity (Smith *et al.*, 1996) displayed by haloruthenium–sulfoxide species has revived interest in such complexes (Rack & Gray, 1999; Cingi *et al.*, 2000) and prompted further scrutiny of the bonding of dmso to Ru. Here, we report the synthesis, characterization and molecular structure of a relevant new complex, $[RuCl_2(apy)(dmso)_2]$, (I), containing 2-acetylpyridine (apy) as the ancillary ligand.



(I)

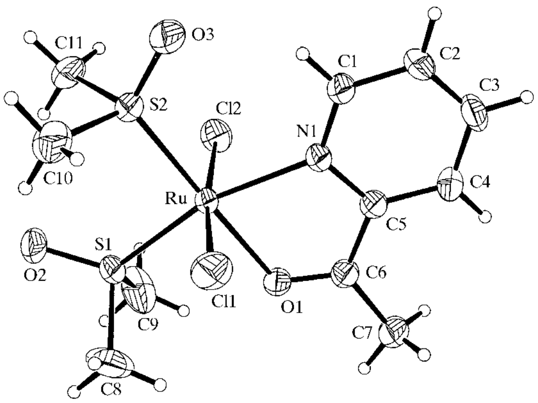


Figure 1
The molecular structure of (I) with the atom-numbering scheme. Displacement ellipsoids are drawn at the 40% probability level and H atoms are shown as small spheres of arbitrary radii.

The molecular structure of (I) is depicted in Fig. 1. The bond parameters associated with the Ru^{II} centre indicate a distorted octahedral $NOCl_2S_2$ coordination sphere around the metal ion. The two *S*-coordinated dmso molecules and the two Cl^- ions in the coordination sphere are found to be *cis* and *trans* pairs, respectively. The two remaining *cis* sites are occupied by the chelating *N*,*O*-donor 2-acetylpyridine, with a chelate bite angle of 76.59 (13)°.

The Ru—O [2.084 (3) Å] and Ru—N [2.122 (3) Å] bond lengths in (I) are similar to those of known Ru^{II} to keto-O (Basuli *et al.*, 2000) and pyridine-N bonds (Bellachioma *et al.*, 1998; Sengupta *et al.*, 2001). The Ru—Cl distances of 2.3753 (16) and 2.3977 (16) Å are unexceptional (Cingi *et al.*, 2000; Alessio *et al.*, 2000).

The Cl1—Ru—Cl2 bond angle of 173.35 (4)° deviates noticeably from the ideal value of 180°. The deviation of the S1—Ru—S2 bond angle [94.98 (6)°] from 90° is most probably due to steric repulsion between the dmso molecules, with the larger angle being accommodated by the small chelate angle of the apy ligand.

The Ru—S bond lengths are significantly different: Ru—S1 = 2.2520 (15) Å and Ru—S2 = 2.225 (2) Å. The longer value is possibly the consequence of the better *trans*-directing ability of the pyridine N atom compared with that of the keto O atom. However, in the coordinated dmso molecules of (I), the corresponding S—O bond lengths [1.472 (3) and 1.461 (4) Å] are comparable. In general, the Ru—S and S—O bond lengths in (I) are well within the range reported for other Ru^{II} complexes containing *S*-coordinated dmso (Alessio *et al.*, 1988, 2000; Cingi *et al.*, 2000).

Experimental

A mixture of *trans*-$[Ru(dmso)_4Cl_2]$ (200 mg, 0.41 mmol) and 2-acetylpyridine (0.14 ml, 1.25 mmol) in methanol (30 ml) was refluxed for 8 h. The clear purple reaction mixture was evaporated to dryness. The dark solid obtained was dissolved in a minimum volume of dichloromethane, followed by the addition of excess hexane. The

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complex which precipitated was collected by filtration and purified on a neutral alumina column. The first purple band was eluted with a dichloromethane–methanol (50:1) mixture. This eluant was collected and evaporated to dryness. The yield of the title complex, (I), thus obtained was 60 mg (32%). Single crystals of (I) were grown by slow evaporation of a dichloromethane–hexane (1:1) solution. Analysis calculated for $C_{11}H_{19}Cl_2NO_3RuS_2$: C 29.40, H 4.26, N 3.12%; found: C 29.17, H 4.39, N 2.91%; selected IR bands (cm^{-1}): 3017 (*m*), 1591 (*w*), 1561 (*w*), 1410 (*m*), 1371 (*m*), 1329 (*m*), 1310 (*m*), 1254 (*m*), 1175 (*w*), 1092 (*s*), 1045 (*w*), 1011 (*s*), 974 (*m*), 918 (*w*), 789 (*s*), 719 (*m*), 681 (*s*), 637 (*w*), 600 (*w*), 426 (*s*); electronic spectroscopic data in CH_2Cl_2 (nm, $dm^3\ mol^{-1}\ cm^{-1}$): 537 (2140), 341 (1410), 282 (6970); ^{1}H NMR (200 MHz, $CDCl_3$, δ, p.p.m.): 3.06 [*s*, 3H, $C(CH_3)$], 3.53 [*s*, 6H, $S(CH_3)_2$], 3.55 [*s*, 6H, $S(CH_3)_2$], 7.83 (*t*, 1H), 8.07 (*t*, 1H), 8.26 (*d*, 1H), 10.56 (*d*, 1H); cyclic voltammetric data (*versus* F_c^+/F_c) at a Pt electrode in CH_2Cl_2 ($E_{1/2}$, V, ΔE_p, mV): 0.69 (260), −1.53 (140).

Crystal data

$[RuCl_2(C_7H_7NO)(C_2H_6OS)_2]$
$M_r = 449.36$
Triclinic, $P\overline{1}$
$a = 8.177$ (5) Å
$b = 8.214$ (3) Å
$c = 14.456$ (6) Å
$\alpha = 84.69$ (3)°
$\beta = 81.13$ (4)°
$\gamma = 63.53$ (5)°
$V = 858.6$ (7) Å^3

$Z = 2$
$D_x = 1.738$ Mg m^{-3}
Mo $K\alpha$ radiation
Cell parameters from 25 reflections
$\theta = 9.6$–10.7°
$\mu = 1.47$ mm^{-1}
$T = 298$ K
Rectangular block, dark brown
0.48 × 0.44 × 0.28 mm

Data collection

Enraf–Nonius MACH3 four-circle diffractometer
ω scans
Absorption correction: ψ scan (*WinGX*; Farrugia, 1999)
$T_{min} = 0.386$, $T_{max} = 0.662$
4006 measured reflections
3934 independent reflections
3300 reflections with $I > 2\sigma(I)$

$R_{int} = 0.003$
$\theta_{max} = 27.5°$
$h = 0 \rightarrow 10$
$k = -9 \rightarrow 10$
$l = -18 \rightarrow 18$
3 standard reflections
frequency: 90 min
intensity decay: none

Table 1
Selected geometric parameters (Å, °).

Ru—O1	2.084 (3)	Ru—S2	2.225 (2)
Ru—N1	2.122 (3)	Ru—Cl1	2.3753 (16)
Ru—S1	2.2520 (15)	Ru—Cl2	2.3977 (16)
O1—Ru—N1	76.59 (13)	N1—Ru—Cl2	86.33 (10)
O1—Ru—S1	86.62 (10)	S1—Ru—S2	94.98 (6)
O1—Ru—S2	177.91 (9)	S1—Ru—Cl1	93.94 (6)
O1—Ru—Cl1	87.16 (11)	S1—Ru—Cl2	92.21 (6)
O1—Ru—Cl2	90.69 (11)	S2—Ru—Cl1	91.38 (6)
N1—Ru—S1	163.12 (10)	S2—Ru—Cl2	90.60 (6)
N1—Ru—S2	101.85 (11)	Cl1—Ru—Cl2	173.35 (4)
N1—Ru—Cl1	87.05 (10)		

Refinement

$R = 0.040$
$wR = 0.118$
$S = 1.03$
3934 reflections
186 parameters
H-atom parameters constrained

$w = 1/[\sigma^2(F_o^2) + (0.071P)^2 + 1.433P]$
where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} = 0.001$
$\Delta\rho_{max} = 1.22$ e Å^{-3}
$\Delta\rho_{min} = -0.91$ e Å^{-3}

The H atoms of the methyl groups were located from difference Fourier syntheses and refined as part of rigid rotating groups, with C—H = 0.96 Å and $U_{iso}(H) = 1.5U_{eq}(C)$. The remaining, aromatic, H atoms were placed geometrically and refined using a riding model, with C—H = 0.93 Å and $U_{iso}(H) = 1.2U_{eq}(C)$.

Data collection: *CAD*-4 *Software* (Enraf–Nonius, 1989); cell refinement: *CAD*-4 *Software*; data reduction: *WinGX* (Farrugia, 1999); program(s) used to solve structure: *SHELXS*97 (Sheldrick, 1997); program(s) used to refine structure: *SHELXL*97 (Sheldrick, 1997); molecular graphics: *ORTEX*-6*a* (McArdle, 1995); software used to prepare material for publication: *SHELXL*97.

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: BM1490). Services for accessing these data are described at the back of the journal.

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