# metal-organic papers

## mer-(2,2′-Bipyridine)trichloro(tetramethylene sulfoxide)ruthenium(III) dichloromethane solvate

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The title compound, mer-[RuCl$_3$(C$_{10}$H$_8$N$_2$)(C$_4$H$_8$OS)]·CH$_2$Cl$_2$ or mer-[RuCl$_3$(bpy)(TMSO)]·CH$_2$Cl$_2$, has the TMSO ligand coordinated through the S atom, with an Ru—S distance of 2.3042 (7) Å. The Ru—Cl distances are in the range 2.3324 (7)–2.3649 (8) Å, with the longest trans to N. The solvent molecule is ordered.

## Comment

Seeking to substitute one of the ligands in the title complex mer-[RuCl$_3$(bpy)(TMSO)] (bpy is 2,2′-bipyridine), (I), with N,N-diethyl-4-nitrosoaniline during the course of our general interest in Ru–halide TMSO complexes, the dichloromethane solvate of the starting material was recovered in crystalline form, as described in the *Experimental* section. Crystal structure analysis revealed that N,N-diethyl-4-nitrosoaniline did not substitute any of the ligands in the parent compound, presumably for steric reasons. Nevertheless, the results are of interest in view of the small amount of structural data available on Ru[III]–TMSO complexes. We have also recently reported the structure of the unsolvated compound (Srivastava & Fronczek, 2005).



(I)
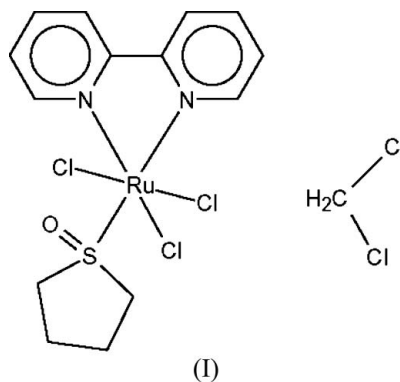
The TMSO ligand, which may be either S- or O-coordinated, coordinates via the S atom in this case, with the S=O bond anti to the central Ru—Cl bond, as was observed in the unsolvated compound (Srivastava & Fronczek, 2005). The bite angle of the bidentate bipyridine, N1—Ru—N2, is 78.49 (8)°, typical of bpy coordinated to second or third row transition metals (Constable, 1989; Constable et al., 2003). This also agrees well with the bite angle of 78.16 (9)° in the unsolvated structure. The Ru—N bond lengths are slightly shorter than the typical Ru[II]—N(bpy) distance of 2.099 Å (Garas et al., 2000; Wang et al., 1999), as expected from the smaller radius of Ru[III]. The Ru—N1 distance, trans to Cl, is shorter than Ru—N2, trans to TMSO, by an amount of marginal statistical significance. However, the difference is probably real, as it was
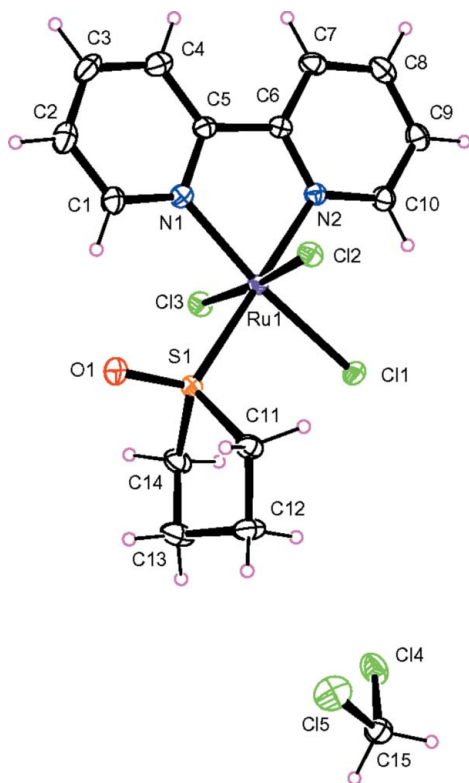
**Figure 1**
The structure of the asymmetric unit of (I), with dispacement ellipsoids at the 50% probability level.

nitrosoaniline (0.25 mmol), and the resulting solution was stirred at room temperature for 25 h. The solvent was removed under reduced pressure, triturated with diethyl ether (4 × 5 ml) and vacuum dried. On recrystallization from a $CH_2Cl_2$/hexane mixture (5:1 $v/v$), the title solvate was obtained as an orange crystalline solid.

*Crystal data*

| | |
|---|---|
| $[RuCl_3(C_{10}H_8N_2)(C_4H_8OS)]\cdot$ $CH_2Cl_2$ | $D_x = 1.810$ Mg m$^{-3}$ |
| | Mo $K\alpha$ radiation |
| $M_r = 552.69$ | Cell parameters from 8203 |
| Monoclinic, $P2_1/c$ | reflections |
| $a = 12.804$ (2) Å | $\theta = 2.5–33.7°$ |
| $b = 10.139$ (2) Å | $\mu = 1.54$ mm$^{-1}$ |
| $c = 15.734$ (2) Å | $T = 110$ K |
| $\beta = 96.703$ (11)° | Prism, orange |
| $V = 2028.6$ (6) Å$^3$ | $0.15 \times 0.12 \times 0.10$ mm |
| $Z = 4$ | |

*Data collection*

| | |
|---|---|
| Nonius KappaCCD diffractometer | 56386 measured reflections |
| (with an Oxford Cryosystems | 8048 independent reflections |
| Cryostream cooler) | 5695 reflections with $I > 2\sigma(I)$ |
| $\omega$ scans | $R_{int} = 0.044$ |
| Absorption correction: multi-scan | $\theta_{max} = 33.7°$ |
| *HKL SCALEPACK* | $h = -19 \rightarrow 19$ |
| (Otwinowski & Minor 1997) | $k = -15 \rightarrow 15$ |
| $T_{min} = 0.796$, $T_{max} = 0.857$ | $l = -24 \rightarrow 23$ |

*Refinement*

| | |
|---|---|
| Refinement on $F^2$ | $w = 1/[\sigma^2(F_o^2) + (0.0297P)^2$ |
| $R[F^2 > 2\sigma(F^2)] = 0.041$ | $+ 1.6323P]$ |
| $wR(F^2) = 0.086$ | where $P = (F_o^2 + 2F_c^2)/3$ |
| $S = 1.06$ | $(\Delta/\sigma)_{max} = 0.001$ |
| 8048 reflections | $\Delta\rho_{max} = 2.23$ e Å$^{-3}$ |
| 226 parameters | $\Delta\rho_{min} = -1.01$ e Å$^{-3}$ |
| H-atom parameters constrained | |

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

| | | | |
|---|---|---|---|
| Ru1—N1 | 2.077 (2) | Ru1—Cl1 | 2.3649 (8) |
| Ru1—N2 | 2.086 (2) | S1—O1 | 1.4781 (19) |
| Ru1—S1 | 2.3042 (7) | Cl4—C15 | 1.769 (3) |
| Ru1—Cl3 | 2.3324 (7) | Cl5—C15 | 1.768 (3) |
| Ru1—Cl2 | 2.3414 (7) | | |
| | | | |
| N1—Ru1—N2 | 78.49 (8) | Cl2—Ru1—Cl1 | 92.27 (2) |
| Cl3—Ru1—Cl1 | 93.49 (2) | | |
| | | | |
| N1—Ru1—S1—O1 | −3.66 (12) | | |

also observed in the unsolvated structure. The short Ru—N1 distance is accompanied by a Ru—Cl1 distance *trans* to it, which is somewhat longer than the two Ru—Cl distances *trans* to each other.

The Ru—S bond is significantly shorter than the average value of 2.3866 Å found for *mer*-[RuCl$_3$(TMSO)$_3$] (Yapp *et al.*, 1990) and other Ru$^{III}$–S compounds, *trans* to TMSO-S in the precursor (Alessio *et al.*, 1990, 1991; Calligaris *et al.*, 1993; Jaswal *et al.*, 1990). The Ru—S bond distances in the present compound do not show any substantial reduction with respect to *cis*-[RuCl$_2$(TMSO)$_4$] (Yapp *et al.*, 1990) and other Ru$^{II}$–S bond distances (Alessio *et al.*, 1990, 1991; Wang *et al.*, 1999). The Ru—S bond length depends upon the oxidation state and on the nature of coordinating *trans* ligands. The decrease in Ru—S bond length from Ru$^{II}$ to Ru$^{III}$ is partially due to the $\pi$-back-bonding contribution in the Ru—TMSO bond (Calligaris *et al.*, 1996; Srivastava *et al.*, 2004; Iengo *et al.*, 1999). The S—O bond length, however, is shorter than in crystalline TMSO (1.527 Å; Dodge *et al.*, 1972; Jaswal *et al.*, 1990), suggesting a significant S—O $\pi$-bonding, resulting from S-to-metal electron-density transfer (Davies, 1981; Jaswal *et al.*, 1990).

The solvent molecule is ordered, with statistically indistinguishable C—Cl distances.

H atoms were placed in idealized positions, with C—H bond distances in the range 0.95–0.99 Å, and thereafter treated as riding. Displacement parameters were assigned as $U_{iso}$(H) = $1.2U_{eq}$ of the attached atom. The largest residual difference-map peak is 0.73 Å from the Ru atom and the deepest hole is 0.71 Å from the Ru atom.

Data collection: *COLLECT* (Nonius, 2000); cell refinement: *SCALEPACK* (Otwinowski & Minor, 1997); data reduction: *SCALEPACK* and *DENZO* (Otwinowski & Minor, 1997); program(s) used to solve structure: *SIR97* (Altomare *et al.*, 1999); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *ORTEP-3 for Windows* (Farrugia, 1997); software used to prepare material for publication: *SHELXL97*.

## Experimental

To a homogeneous solution of *mer*-[RuCl$_3$(bpy)(TMSO)] (0.23 mmol) in ClCH$_2$CH$_2$Cl (35 ml) was added solid *N,N*-diethyl-4-

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