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[1,3-Bis(2-pyridylimino)isoindolinato-κ^3*N*,*N*′,*N*″]-chloro(1,2-dicyanobenzene-κ*N*)(dimethyl sulfoxide-κ*S*)ruthenium(II)

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Key indicators

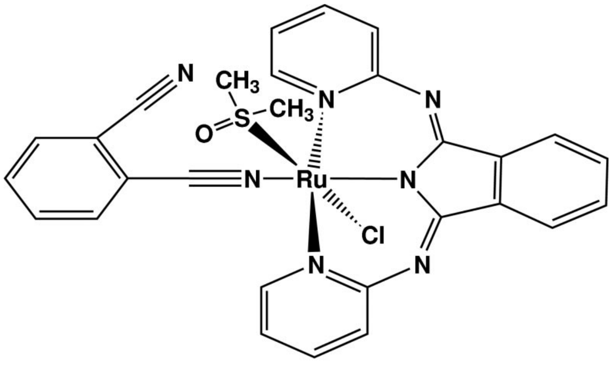
Single-crystal X-ray study
T = 153 K
Mean σ(C–C) = 0.004 Å
R factor = 0.041
wR factor = 0.094
Data-to-parameter ratio = 20.3

For details of how these key indicators were automatically derived from the article, see http://journals.iucr.org/e.

The title compound, [Ru($C_{18}H_{12}N_5$)Cl($C_8H_4N_2$)(C_2H_6OS)], consists of an Ru^{II} atom hexagonally coordinated by a tridendate isoindoline ligand, a Cl atom, the S atom of a dimethyl sulfoxide molecule and an N atom of a CN group of dicyanobenzene. In the crystal structure, a three-dimensional network is built up owing to the presence of weak C—H···O and C—H···Cl intermolecular hydrogen bonds.

Comment

The title compound, (I), was synthesized when attempts were made to prepare the first ruthenium(II) complex of the ligand 1,3-tris(2′-pyridylimino)isoindoline, *L*1, using Ru(dmso)$_4$Cl$_2$ in the metal-to-ligand ratio of 1:2 (dmso is dimethyl sulfoxide). The ligand synthesis involves the reaction of 1,2-dicyanobenzene with 2-aminopyridine (Siegl, 1977). Owing to the similar solubility properties of the final product, *L*1, and the starting materials it was not easy to purify *L*1. The reaction of crude *L*1 with Ru(dmso)$_4$Cl$_2$ in methanol led to the formation of (I). The crystal structure of the free ligand *L*1, (II), has been published recently (Schif, 2004). The molecule is planar, with intramolecular, bifurcated, symmetric hydrogen bonds involving the three N atoms (N1, N3 and N5; Fig. 1). We subsequently also obtained single crystals of (II) and our structure analysis agreed with that reported above.



(I)

The molecular structure of (I) is shown in Fig. 1 and selected geometric parameters are given in Table 1. Atom Ru1 has a reasonably regular octahedral coordination environment. The central Ru—N(isoindoline) bond distance is shorter [1.997 (2) Å] than the Ru—N(pyridine) bond distances [2.111 (2) and 2.094 (2) Å]. The ligand *L*1 in (I), twisting essentially about the bond N4—C13, is less planar than that in (II). The relevant torsion angles involving atoms N2 and N4 are given in Table 1. Within the complex there are

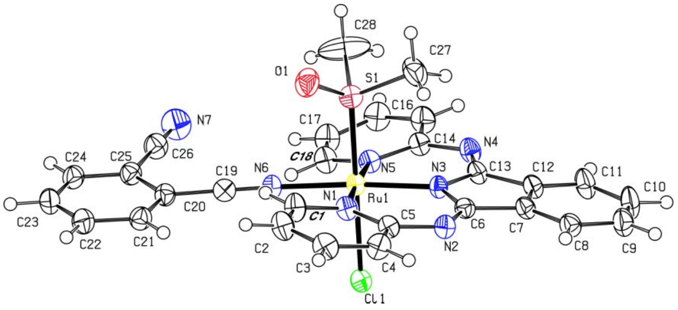


Figure 1
The molecular structure of (I), showing the atomic numbering scheme and displacement ellipsoids at the 50% probability level.

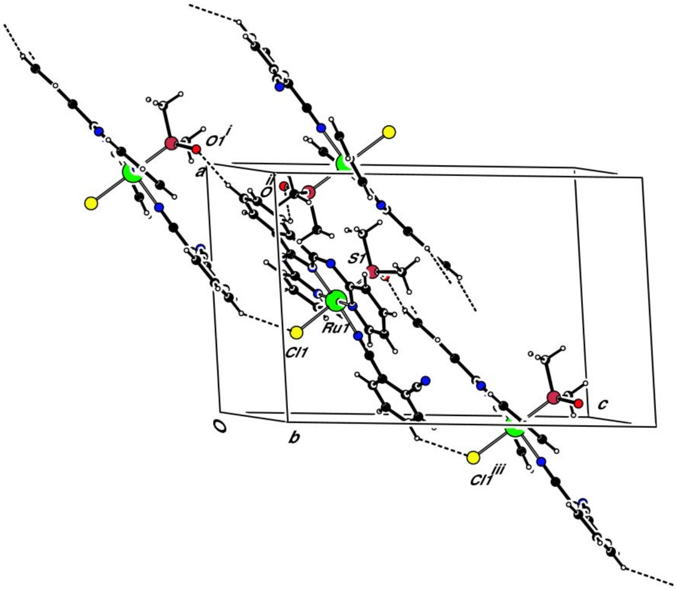


Figure 2
Part of the crystal packing in (I), showing the formation of the hydrogen-bonded (dashed lines) network. [Symmetry codes: (i) $x + \frac{1}{2}, \frac{1}{2} - y, -\frac{1}{2} + z$; (ii) $\frac{3}{2} - x, \frac{1}{2} + y, \frac{1}{2} - z$; (iii) $-\frac{1}{2} + x, \frac{1}{2} - y, \frac{1}{2} + z$.]

two intramolecular C—H···N contacts involving the coordinated cyano N atom, N6, and the H atoms of atoms C1 and C18 of the two pyridine rings of *L*1 (H1···N6 = 2.33 Å and H18···N6 = 2.34 Å).

The dmso molecule coordinates atom Ru1 *via* atom S1, with an Ru1—S1 bond distance of 2.2087 (7) Å. This is shorter than those observed in similar compounds, for example, 2.251 (1) and 2.258 (1) Å in chloro(dimethyl sulfoxide)tris(2-pyridylmethyl)amineruthenium(II) hexafluorophosphate (Bjernemose *et al.*, 2003). The Ru1—Cl1 bond distance [2.4325 (7) Å] is very similar to that in the above-mentioned compound [2.430 (1) and 2.420 (1) Å]. The 1,2-dicyanobenzene ligand coordinates atom Ru1 *via* the N atom of one cyano group, the Ru1—N6 bond distance being 2.027 (2) Å. This mono-coordination mode of 1,2-dicyanobenzene with ruthenium has never been observed previously, but examples exist with zirconium (Kubiak & Ejsmont, 1998), titanium (Berhalter & Thewalt, 1987) and rhenium (Derringer *et al.*, 1991).

In the crystal structure, the molecules are linked by weak intermolecular C—H···O and C—H···Cl hydrogen bonds (Table 2) to form a three-dimensional network, as shown in Fig. 2.

Experimental

The precursor complex Ru(dmso)$_4$Cl$_2$ was prepared according to the procedure of Evans *et al.* (1973). The ligand (*L*1) was prepared following the procedure described by Siegl (1977). Complex (I) was prepared by adding Ru(dmso)$_4$Cl$_2$ (0.05 g, 0.1 mmol) to the ligand (*L*1; 0.06 g, 0.2 mmol) in methanol (14 ml). The mixture was allowed to reflux for 10 h and was then cooled to ambient temperature. The solution was filtered and the filtrate was allowed to evaporate slowly in air. In about a week, dark-red block-like X-ray quality crystals of the title complex were obtained. X-ray analysis indicated that the original ligand sample was not pure, but contaminated by 1,2-dicyanobenzene used in the synthesis of *L*1.

Crystal data

[Ru(C$_{18}$H$_{12}$N$_5$)Cl(C$_8$H$_4$N$_2$)-(C$_2$H$_6$OS)]
M_r = 641.11
Monoclinic, $P2_1/n$
a = 11.5299 (5) Å
b = 12.9081 (5) Å
c = 17.4774 (9) Å
β = 94.538 (4)°
V = 2593.0 (2) Å^3
Z = 4
D_x = 1.642 Mg m^{-3}
Mo *K*α radiation
Cell parameters from 30 303 reflections
θ = 1.8–29.6°
μ = 0.83 mm^{-1}
T = 153 (2) K
Block, dark red
0.35 × 0.24 × 0.10 mm

Data collection

Stoe IPDS-II diffractometer
ω scan
Absorption correction: multi-scan (*MULscanABS* in *PLATON*; Spek, 2003)
$T_{\min}$ = 0.728, $T_{\max}$ = 0.970
37 823 measured reflections
7199 independent reflections
6291 reflections with $I > 2\sigma(I)$
$R_{\rm int}$ = 0.043
$\theta_{\max}$ = 29.6°
$h = -15 \rightarrow 15$
$k = -17 \rightarrow 17$
$l = -24 \rightarrow 24$

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)]$ = 0.041
$wR(F^2)$ = 0.094
S = 1.07
7199 reflections
354 parameters
H-atom parameters constrained
$w = 1/[\sigma^2(F_o^2) + (0.0441P)^2 + 3.0086P]$
where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{\max}$ = 0.001
$\Delta\rho_{\max}$ = 0.57 e Å^{-3}
$\Delta\rho_{\min}$ = −0.98 e Å^{-3}

Table 1
Selected geometric parameters (Å, °).

Ru1—Cl1	2.4325 (7)	Ru1—N3	1.997 (2)
Ru1—S1	2.2087 (7)	Ru1—N5	2.094 (2)
Ru1—N1	2.111 (2)	Ru1—N6	2.027 (2)
Cl1—Ru1—S1	179.64 (3)	S1—Ru1—N6	91.00 (6)
Cl1—Ru1—N1	91.54 (6)	N1—Ru1—N3	88.50 (8)
Cl1—Ru1—N3	87.53 (6)	N1—Ru1—N5	176.91 (8)
Cl1—Ru1—N5	87.57 (6)	N1—Ru1—N6	90.40 (8)
Cl1—Ru1—N6	88.89 (6)	N3—Ru1—N5	88.51 (8)
S1—Ru1—N1	88.12 (6)	N3—Ru1—N6	176.22 (8)
S1—Ru1—N3	92.58 (6)	N5—Ru1—N6	92.54 (8)
S1—Ru1—N5	92.78 (6)		
C5—N2—C6—N3	−2.7 (4)	C14—N4—C13—N3	−10.0 (4)
C6—N2—C5—N1	1.5 (4)	C13—N4—C14—N5	−2.6 (4)

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

	D—H	H···A	D···A	D—H···A
C9—H9···O1^{i}	0.95	2.34	3.264 (3)	165
C11—H11···O1^{ii}	0.95	2.59	3.241 (4)	126
C23—H23···Cl1^{iii}	0.95	2.80	3.557 (3)	137

Symmetry codes: (i) $x+\frac{1}{2}, -y+\frac{1}{2}, z-\frac{1}{2}$; (ii) $-x+\frac{3}{2}, y+\frac{1}{2}, -z+\frac{1}{2}$; (iii) $x-\frac{1}{2}, -y+\frac{1}{2}, z+\frac{1}{2}$.

H atoms were included in calculated positions and treated as riding atoms, with C—H = 0.95–0.98 Å and with $U_{\rm iso}$(H) = 1.2$U_{\rm eq}$(C) or 1.5$U_{\rm eq}$(C). The methyl atom, C28, of the dmso molecule undergoes considerable thermal vibration but attempts to refine it as a split atom were not successful.

Data collection: *X-AREA* (Stoe & Cie, 2004); cell refinement: *X-AREA*; data reduction: *X-RED*32 (Stoe & Cie, 2004); program(s) used to solve structure: *SHELXS*97 (Sheldrick, 1990); program(s) used to refine structure: *SHELXL*97 (Sheldrick, 1997); molecular graphics: *PLATON* (Spek, 2003); software used to prepare material for publication: *SHELXL*97.

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