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The crystal and molecular structure of bis(2-pyridinethiolato)-(bicyclo[2.2.1]hepta-1,4-diene)ruthenium(II)

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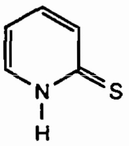
Abstract

The crystal and molecular structore of the complex [Ru(nbd)L_2] (nbd = bicyclo[2.2.1]hepta-1,4-diene; HL = 2(1*H*)-pyridinethione) are described. The ruthenium centre is six-coordinate with a *transoid* arrangement of the two sulfur atoms of two chelating bidentate L ligands.

Introduction

2(1*H*)-Pyridinethione (HL) has attracted some interest as a ligand for transition metals and has been shown to adopt a wide range of different bonding modes [1, 2]. Although complexes with many transition metal ions have been reported, only a few examples of ruthenium compounds have been described [3–12]. We have recently become interested in the ways in which the bonding mode of ligands such as HL are dependent upon the metal centre to which they are coordinated [6, 13, 14], and in this paper we wish to report the crystal and molecular structure of the complex [RuL_2(nbd)] (nbd = bicylo[2.2.1]hepta-1,4-diene).



HL

Experimental

The complex [RuL_2(nbd)] was prepared as described previously [6, 11].

X-ray crystallography of [RuL_2(nbd)]

Orange–red crystals of [RuL_2(nbd)] were obtained by slow evaporation of a dichloromethane solution of the complex. The crystals were stable in air, and several were mounted on glass fibres. The space group and unit cell dimensions were derived from preliminary Weissenberg photography. Pertinent crystallographic data are given in Table 1. The data were recorded on a four-circle diffractometer and Lorentz polarization corrections

TABLE 1. Crystal data for [RuL_2(nbd)]

Formula	$C_{17}H_{16}N_2RuS_2$
Formula weight	413.51
Space group	$P\bar{1}$ (No. 2)
a (Å)	9.157(2)
b (Å)	13.946(2)
c (Å)	14.163(2)
α (°)	109.39(1)
β (°)	101.28(2)
γ (°)	91.98(1)
V (Å^3)	1663
Z	4
F(000)	832
D_{calc} (g/cm^3)	1.65
Crystal size (mm)	0.12 × 0.28 × 0.48
μ(Mo Kα) (cm^{-1})	11.30
Data collection instrument	Stoe-Siemens four-circle
Radiation	Mo Kα ($\lambda = 0.7107$ Å)
Data collection range (°)	$5 \leqslant 2\theta \leqslant 50$
Temperature (°C)	20
No. unique data	5840
Total with $F \geqslant 4\sigma(F)$	5168
R^a	0.0315
R'^b	0.0368
Weighting scheme	$w = 1/[\sigma^2F + 0.0007F^2]$
Largest peak (e/Å^3)	0.65

$^aR = \Sigma[|F_o| - |F_c]/\Sigma|F_o|$. $^bR' = \Sigma w^{\frac{1}{2}}[|F_o| - |F_c|]/\Sigma w^{\frac{1}{2}}|F_o|$.

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TABLE 2. Selected bond lengths (Å) and bond angles (°) for $[RuL_2(nbd)]$

Ru(1)–S(11)	2.426(1)	Ru(1)–N(11)	2.106(4)
Ru(1)–S(12)	2.427(1)	Ru(1)–N(12)	2.104(3)
Ru(1)–C(111)	2.178(4)	Ru(1)–C(112)	2.171(5)
Ru(1)–C(114)	2.174(4)	Ru(1)–C(115)	2.173(4)
S(11)–Ru(1)–N(11)	67.8(1)	S(11)–Ru(1)–S(12)	149.9(1)
S(11)–Ru(1)–N(12)	91.3(1)	N(11)–Ru(1)–S(12)	91.2(1)
N(11)–Ru(1)–N(12)	92.4(1)	S(12)–Ru(1)–N(12)	67.4(1)

applied. Empirical absorption corrections were applied.

The positions of the ruthenium atoms were determined from the Patterson function and all remaining non-hydrogen atoms were determined from subsequent Fourier difference syntheses. The structure was refined (Ru, C, N and S anisotropic, H in idealized positions (C–H, 1.08 Å)) and allowed to ride on relevant C, to $R = 0.0315$ ($R_w = 0.0368$). A final difference map showed no significant regions of electron density greater than 0.65 $Å^{-3}$. Calculations were carried out using the program SHELX on the University of Cambridge IBM 370/165 computer [15]. Selected dimensions within the coordination sphere are presented in Table 2. See also 'Supplementary material'.

Results and discussion

In view of the versatility of ambidentate ligands such as HL there has been surprisingly little interest in their ruthenium complexes. The reaction of ruthenium blue solutions derived from 'ruthenium trichloride' with HL results in the formation of the diamagnetic compound $[\{RuL_2Cl_2\}_n]$, which reacts with PPh_3 to yield $[RuL_2(PPh_3)_2]$ [8]. The latter complex has been structurally characterized, and shown to contain two bidentate chelating L ligands with *transoid* sulfur atoms and *cis* phosphine groups [7]. Single isomers of the complexes $[Ru(cod)L_2]$ (cod = 1,5-cyclooctadiene) and $[Ru(nbd)L_2]$ are readily prepared by the reaction of $[\{Ru(diene)Cl_2\}_n]$ (diene = cod or nbd) with HL [6, 11]. The alkylation of the two complexes $[Ru(diene)L_2]$ (diene = cod or nbd) has been investigated [6]. A range of phosphine complexes has been prepared by the reaction of HL with a variety of organometallic intermediates [4, 9, 10, 12]. Ruthenium(II) complexes have been obtained by the oxidative addition of di(2-pyridyl)disulfide to $[Ru(CO)_3(PPh_3)_2]$, and the complex $[Ru(CO)_2(PPh_3)L_2]$ has been structurally characterized [9]. The complexes $[RuCl_2(CO)_2(HL)_2]$ [5], $[Ru(Hedta)(HL)]$ and $[Ru(edta)(L)]^{2-}$ (H_4edta = 1,2-diaminoethane-*N,N,N',N'*-tetraacetic acid) [3] have also been reported.

It was known that single isomers of the complexes $[Ru(diene)L_2]$ (diene = cod or nbd) could be obtained from the reaction of $[\{Ru(diene)Cl_2\}_n]$ (diene = cod or nbd) with HL in *N,N'*-dimethylformamide in the presence of anhydrous sodium carbonate [6, 11], and we proposed a structure in which the metal was in a distorted octahedral environment with the two sulfur atoms *trans* to each other on the basis of ^1H and ^{13}C NMR studies [6]. In order to confirm these conclusions we have determined the crystal and molecular structure of the complex $[Ru(nbd)L_2]$.

The molecular structure of one of the two crystallographically independent molecules of $[Ru(nbd)L_2]$ in the unit cell is shown in Fig. 1. Relevant crystallographic details and selected dimensions within the coordination sphere are presented in Tables 1 and 2. Each molecule possesses a distorted octahedral geometry with a *transoid* arrangement of the sulfur atoms. The Ru–S distances (2.426(1), 2.427(1) Å) closely resemble (but are significantly shorter than) those observed for the bidentate L ligands in the complexes $[RuL_2(CO)_2(PPh_3)]$. (2.452 Å) [9, 10], $[RuL_2(CO)(PPh_3)]$ (2.428, 2.422 Å) [9, 10] and $[RuL_2(PPh_3)_2]$ (2.433, 2.437 Å) [7], and are considerably longer than the Ru–S distance observed to the monodentate S-bonded ligand in $[RuL_2(CO)_2(PPh_3)]$ (2.418 Å) [9, 10]. The Ru–N distances of 2.106(4) and 2.104(3) Å are also comparable but shorter than those previously reported for $[RuL_2(CO)_2(PPh_3)]$ (2.114 Å) [9, 10], $[RuL_2(CO)(PPh_3)]$ (2.138, 2.118 Å) [9, 10] and $[RuL_2(PPh_3)]$ (2.116, 2.122 Å) [7]. We attribute the shortening of these distances to the increased electropositive character of the ruthenium centre coordinated to the strongly π-accepting diene ligand. The bite angles of the ligands (67.8(1), 67.4(1)°) are similar to those observed in $[RuL_2(CO)_2(PPh_3)]$ (67.6°) [9, 10], $[RuL_2(CO)(PPh_3)]$ (67.8, 67.5°) [9, 10] and $[RuL_2(PPh_3)_2]$ (66.6, 67.6°) [7].The ruthenium–diene bonding is unremarkable.

The two sulfur atoms lie *trans* to each other, and make a S(11)–Ru(1)–S(12) angle of 149.9°. This *trans* arrangement of the sulfur atoms has now been observed in all complexes containing an $\{RuL_2\}$ group, although the angles vary from 158° in $[RuL_2(CO)(PPh_3)]$ [9, 10] to 154.7° in $[RuL_2(PPh_3)]$ [7]. This does not appear to represent a simple *trans* effect, since the complex $[RuL_2(CO)_2(PPh_3)]$ (the precursor to $[RuL_2(CO)(PPh_3)]$ which contains one bidentate and one monodentate L ligand exhibits a *cis* arrangement of the sulfur atoms [9, 10]. The overall structure appears to be favoured by a combination of

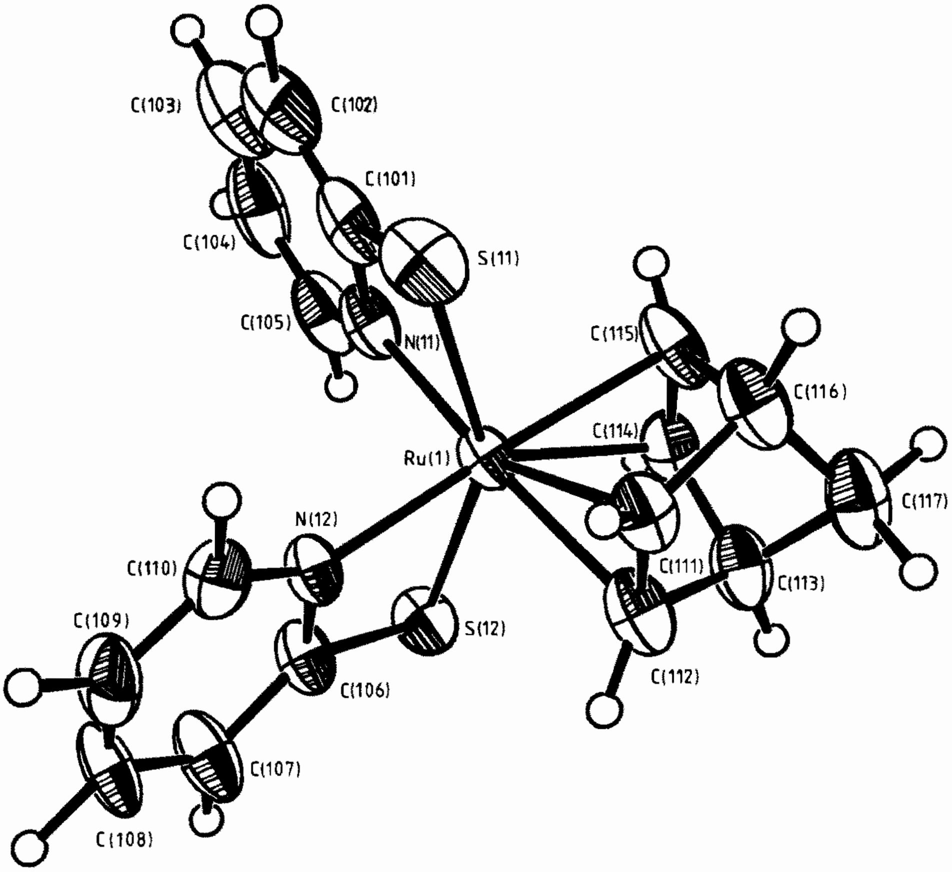

Fig. 1. The molecular structure of [Ru(nbd)L_2] showing the numbering scheme adopted.

electronic and steric effects associated with the chelating ligands.

The crystal and molecular structure of [Ru(nbd)L_2] confirms the geometry assigned on the basis of NMR studies. We are currently further investigating the features which favour this geometry.

Supplementary material

Tables of all final coordinates and thermal parameters, bond lengths, bond angles, hydrogen atom coordinates and tables of observed and calculated structure factors are available from the authors.

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