

### An O-Bonded Nitrito Nitrosyl Schiff Base Complex: X-Ray Molecular Structure of $[\text{Ru}(\text{sal}_2\text{en})(\text{NO}_2)(\text{NO})]$

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Although there have been many reports in the literature of the preparation of Schiff base complexes of the transition metals, the reaction of such complexes with nitric oxide has been studied in only a few cases. The reaction of metal- $\text{N,N}'$ -ethylenebis(salicylideneiminato),  $\text{M}(\text{sal}_2\text{en})$ , complexes with nitric oxide have been shown to give  $[\text{M}(\text{sal}_2\text{en})(\text{NO})]$  ( $\text{M} = \text{Fe}$  [1],  $\text{Co}$  [2]),  $[\text{MO}(\text{sal}_2\text{en})_2\text{O}_2]$  [3] or  $[\text{M}(\text{OH})(\text{sal}_2\text{en})]$  [4] ( $\text{M} = \text{Mn}$ ), and in the presence of air 5,5-dinitrosal<sub>2</sub>en complexes ( $\text{M} = \text{Ni}, \text{Cu}$ ) [5].

The reaction of a warm (60 °C) solution of  $[\text{Ru}(\text{sal}_2\text{en})(\text{PPh}_3)_2]$  [6] in tetrahydrofuran (THF) with nitric oxide gives an orange-red solid of stoichiometry  $[\text{Ru}(\text{sal}_2\text{en})(\text{NO})]_2\text{O}$  and a pale green-red solution from which burgundy coloured needles were isolated. To determine the exact nature of these crystals an X-ray single-crystal analysis was carried out.

Crystals of the title complex, in the form of a tetrahydrofuran solvate of ideal stoichiometry  $[\text{Ru}(\text{sal}_2\text{en})(\text{NO}_2)(\text{NO})] \cdot \text{THF}$ , are monoclinic, with unit-cell dimensions  $a = 18.668(2)$ ,  $b = 19.178(2)$ ,  $c = 12.739(1)$  Å,  $\beta = 105.87(1)^\circ$ , space group is  $\text{P}2_1/\text{n}$  and  $Z = 8$ . A total of 3552 independent reflections were measured (to  $\theta = 45^\circ$ ) on a Siemens four-circle automatic diffractometer. The structure was solved by Patterson and Fourier methods, and least-squares refinement has reached  $R = 0.043$ .

There are no significant differences between the two crystallographically independent complex molecules in the unit cell. These are monomeric and have a slightly distorted octahedral coordination geometry. The  $\text{sal}_2\text{en}$  group acts as a relatively planar tetradentate ligand, while a linear nitrosyl and a nitrito group are *trans* to each other. Figure 1 shows the molecular structure. Average bond lengths are:  $\text{Ru}-\text{O}(\text{sal}_2\text{en})$  2.025 Å,  $\text{Ru}-\text{N}(\text{sal}_2\text{en})$  2.005 Å,  $\text{Ru}-\text{N}(\text{nitrosyl})$  1.713 Å, and  $\text{Ru}-\text{O}(\text{nitrito})$  2.011 Å.

The nitrito group is bonded to ruthenium *via* one of its oxygen atoms rather than through the nitrogen. It is best to regard it as an  $\text{NO}_2^-$  ligand; the mean  $\text{ONO}$  angle of  $116.5^\circ$  is typical ( $115^\circ$ ) for this group and may be compared [7] to  $134^\circ$  for  $\text{NO}_2$  and  $180^\circ$  for  $\text{NO}_2^+$ . The whole  $\text{sal}_2\text{en}$  ligand deviates little from planarity – except for the dimethylene

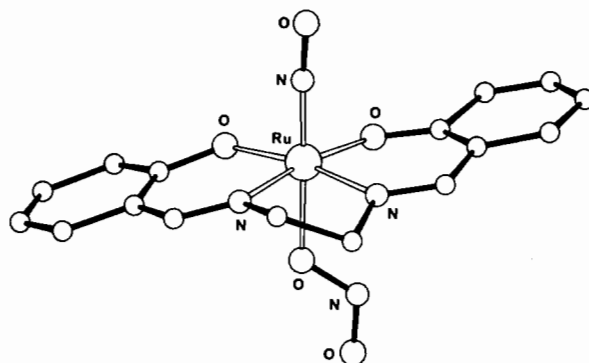


Fig. 1. Molecular structure of  $[\text{Ru}(\text{sal}_2\text{en})(\text{NO}_2)(\text{NO})]$ .

bridge, the maximum deviation is  $< 0.3$  Å. If, however, the ligand is taken to consist of three planes where  $\text{ONNO}$  is the middle plane, then the distortion can best be described in terms of a 'stepped' conformation as defined by Calligaris *et al.* [8]. The tetrahydrofuran solvate molecules are not coordinated, and simply fill up holes in the crystal structure. There are indications that one of the two independent THF molecules may have a less than complete site occupancy. Full crystallographic details will be published separately.

The infrared spectrum of the diamagnetic title complex has a single nitrosyl stretching vibration  $\nu(\text{N}=\text{O})$  at  $1831 \text{ cm}^{-1}$  and antisymmetric  $\text{N}-\text{O}$  vibrations of the  $\text{NO}_2$  ligand  $\nu'_{\text{as}}(\text{N}-\text{O})$  at  $1488, 1507 \text{ cm}^{-1}$ , confirming that the  $\text{NO}_2$  ligand is O-bonded as a nitrite [9] group. The  $^1\text{H}$  n.m.r. spectrum of this complex is mostly as expected for a complex containing a planar  $\text{sal}_2\text{en}$  ligand with a single methine resonance at  $1.77\tau$ , a complex multiplet for the phenyl resonances at  $2.53-3.3\tau$  and, unusually, a singlet resonance due to the methylene protons which in the starting material  $\text{Ru}(\text{sal}_2\text{en})(\text{PPh}_3)_2$  resonate as a multiplet at  $6.2-6.4\tau$ . A singlet methylene resonance observed in the 1.5-cyclooctadiene complex  $[(\text{COD})\text{Rh}]_2\text{sal}_2\text{en}$  has been ascribed to a bridging  $\text{sal}_2\text{en}$  ligand [10], which is clearly not the case with this complex. Analytical data is consistent with the structure:  $[\text{Ru}(\text{sal}_2\text{en})(\text{NO}_2)(\text{NO})] \cdot \text{THF}$  requires: C, 46.6; H, 4.2; N, 10.9%; found: C, 46.6; H, 3.2; N, 11.0%. Molecular weight by osmometry in chloroform: calculated 443; found 486.

Although there are many examples of nitrito-nitrosyl complexes of the transition metals [11] we believe this to be the first example of an O-bonded nitrito-nitrosyl Schiff base complex, in contrast to the N-bonded nitrito-nitrosyl complex containing a macrocyclic ligand recently characterised by Busch [12]. This is also the first structural determination of a ruthenium Schiff base complex.

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