

## The Structure of Nitrosylruthenium Tris-(*NN*-diethyldithiocarbamate): a Complex with a Monodentate Dithiocarbamate Group

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COMPOUNDS  $[\text{Ru}(\text{NO})(\text{S}_2\text{CNR}_2)_3]$  (R = Me and Et), first described by Cambi and Malatesta,<sup>1</sup> appear to contain seven-co-ordinate ruthenium. In order to establish the co-ordination of the metal ion these compounds were examined again. The methyl

compound (m.p. 220—221°) shows strong NO absorption at 1830  $\text{cm}^{-1}$  and the ethyl compound (m.p. 158—159°) at 1803  $\text{cm}^{-1}$ , indicating that the nitrosyl group can be considered as  $\text{NO}^+$  as in  $[\text{Et}_4\text{N}]_2[\text{RuCl}_5(\text{NO})]$  which absorbs<sup>2</sup> at 1830  $\text{cm}^{-1}$

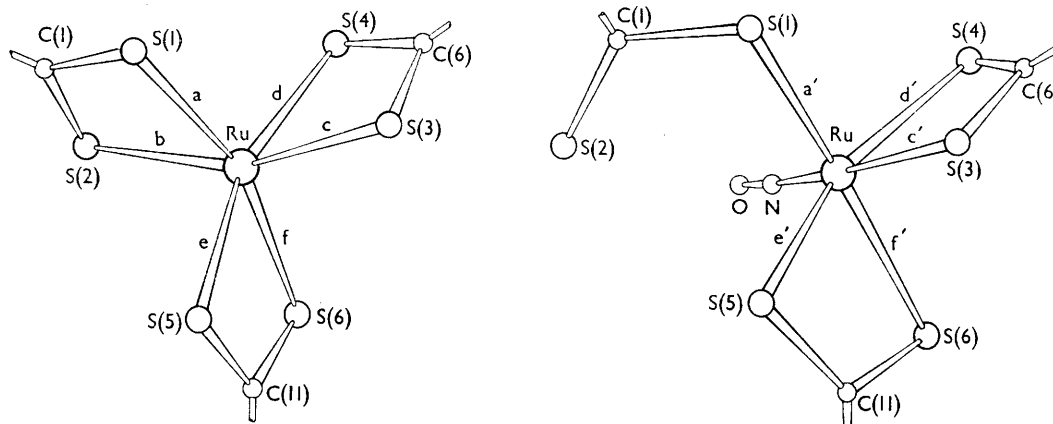


FIGURE The co-ordination spheres of ruthenium tris-(NN-diethylthiocarbamate) and nitrosylruthenium tris-(NN-diethylthiocarbamate). Bond lengths are:  $a = 2.385$ ,  $b = 2.385$ ,  $c = 2.377$ ,  $d = 2.382$ ,  $e = 2.385$ ,  $f = 2.380$  Å and, respectively,  $a' = 2.398$ ,  $c' = 2.415$ ,  $d' = 2.413$ ,  $e' = 2.375$ ,  $f' = 2.403$  Å. In the nitrosyl complex the Ru-S(2) contact distance is 3.633 Å and the Ru-N and N-O bond distances are 1.72 and 1.17 Å respectively. The angle Ru-N-O is  $170^\circ$ .

Comparison of the infrared spectra of  $[\text{Ru}(\text{NO})(\text{S}_2\text{CNR}_2)_3]$  and  $[\text{Ru}(\text{S}_2\text{CNR}_2)_3]^{3+}$  shows that, in addition to the bands present in the simple dithiocarbamates, the nitrosyl compounds reveal bands at 1460–1470, 1410, 1260–1265, 1060–1065, and 970–980  $\text{cm}^{-1}$ . This suggested that one of the dithiocarbamate groups might be acting as a monodentate group because: (i) the presence of nitric oxide in other dithiocarbamate complexes does not appear to cause an increase in the number of bands<sup>4</sup> and (ii) the band at 1460–1470  $\text{cm}^{-1}$  is close to the CN stretch in  $\text{NaS}_2\text{CNMe}_2$  and in  $\text{NaS}_2\text{CNET}_2$ .<sup>4</sup>

Confirmation of this hypothesis was obtained from the X-ray structure determination of  $[\text{Ru}(\text{NO})(\text{S}_2\text{CNET}_2)_3]$ . For the purpose of comparison the structure of  $[\text{Ru}(\text{S}_2\text{CNET}_2)_3]$  was also determined.

$[\text{Ru}(\text{S}_2\text{CNET}_2)_3]$ . Crystals are dark red and crystallize in the monoclinic system;  $a = 14.226 \pm 0.010$ ,  $b = 10.446 \pm 0.010$ ,  $c = 17.947 \pm 0.010$  Å,  $\beta = 116^\circ 48' \pm 5'$ ;  $U = 2380.5$  Å<sup>3</sup>;  $D_m = 1.52 \pm 0.01$  g.cm.<sup>-3</sup> (by flotation);  $Z = 4$ ;  $D_c = 1.523$  g.cm.<sup>-3</sup>;  $F(000) = 1124$ . Space group:  $P2_1/c$  from systematic absences. Data from Weissenberg photographs, Cu- $K_\alpha$  ( $\lambda = 1.5418$  Å) radiation.

$[\text{Ru}(\text{NO})(\text{S}_2\text{CNET}_2)_3]$ . Crystals are dark red and crystallize in the orthorhombic system;  $a = 15.056 \pm 0.010$ ,  $b = 18.392 \pm 0.010$ ,  $c = 18.407 \pm 0.010$  Å;  $U = 5097.1$  Å<sup>3</sup>;  $D_m = 1.50 \pm 0.01$  g.cm.<sup>-3</sup> (by

flotation);  $Z = 8$ ;  $D_c = 1.501$  g.cm.<sup>-3</sup>;  $F(000) = 2368$ . Space group:  $Pbca$  from systematic absences. Data as above.

The two structures were solved by Patterson and Fourier methods, using, respectively, 3259 and 3035 independent reflections. Co-ordinates and anisotropic temperature factors were refined by least-squares to the present set of values, corresponding to  $R = 0.130$  and  $0.084$ , respectively.

The co-ordination spheres of the two complexes are shown in the Figure. The main points of interest in the structure of  $[\text{Ru}(\text{S}_2\text{CNET}_2)_3]$  are: (i) the octahedron is distorted by the requirement of the four-membered rings (S–Ru–S *ca.*  $73^\circ$ ); (ii) the ruthenium–sulphur distances are all practically identical; (iii) the optically active complex is present in the crystal in the form of the racemate, the two optical isomers being related by a glide plane. The principal features of the nitrosyl complex are: (i) it is *six-co-ordinate*, one of the dithiocarbamate groups acting as a monodentate; (ii) the N–O distance (1.17 Å) is indicative that this ligand can be considered as being  $\text{NO}^+$ ; (iii) the ruthenium–sulphur distances vary from 2.375 to 2.415 Å and the nitrosyl group is in *cis*-position to the monodentate dithiocarbamate group; (iv) the complex is optically active and the isomers in the crystal are related by a glide plane.

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<sup>1</sup> L. Cambi and L. Malatesta, *Rend. Ist. Lombardo Sci.*, 1938, **71**, 118. (*Chem. Abs.*, 1940, **34**, 3201–1).

<sup>2</sup> P. Gans, *Chem. Comm.*, 1965, 144.

<sup>3</sup> Compounds  $[\text{Ru}(\text{S}_2\text{CNR}_2)_3]$  (R = Me, Et, Bu<sup>n</sup>) were first described by L. Cambi and L. Malatesta, *Ber.*, 1937, **70**, 2067 and by L. Malatesta, *Gazzetta*, 1938, **68**, 195.

<sup>4</sup> J. Chatt, L. A. Duncanson, and L. M. Venanzi, *Suomen Kem.*, 1956, **29**, B, 75.