

A metal-mediated dimerization of the ligand bis(*N,N*-diethylamino)-carbeniumdithiocarboxylate

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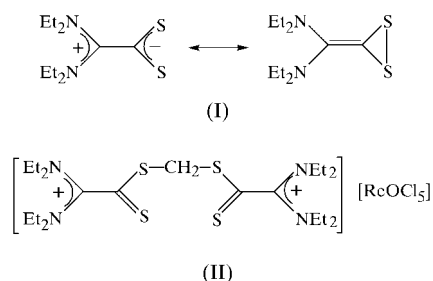
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The title compound, methylene bis[bis(*N,N*-diethylamino)-carbeniumdithiocarboxylate] pentachlorooxorhenium, (C₂₁H₄₂N₄S₄)[ReCl₅O], is the result of an unusual dimerization of the ligand bis(*N,N*-diethylamino)carbeniumdithiocarboxylate [(Et₂N)₂C₂S₂] upon reaction with [ReOCl₃(PPh₃)₂] in chloroform under reflux conditions. The compound was obtained as a dicationic moiety, with the molecular [ReOCl₅]²⁻ anion providing the charge compensation. The planes of the carbenium and thiocarboxylate moieties are nearly perpendicular to one another and the backbone C—C bond length in the N₂CCS₂ group is the same as a normal C—C single-bond length.

Comment

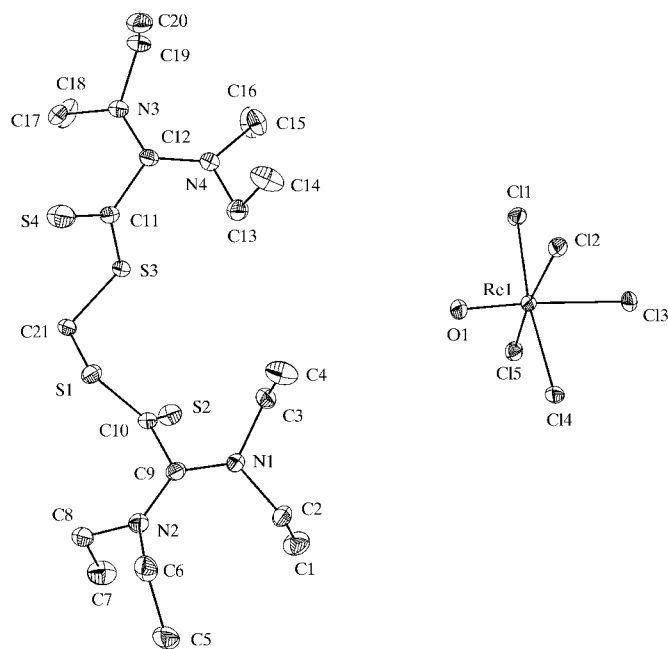
The ligand bis(*N,N*-diethylamino)carbeniumdithiocarboxylate, [(Et₂N)₂C₂S₂], (I), was first synthesized by Nakayama and co-workers (Nakayama & Akiyama, 1992; Nagasawa *et al.*, 1995; Nakayama *et al.*, 2000) and was proposed to possess an interesting inner-salt structure, in which the positive and negative charges are delocalized on the NCN and SCS moieties, although the structure can be drawn as canonical contributions between an inner-salt form and a neutral form.



In previous X-ray structural studies of the tricarbonyl-rhenium complexes with ligand (I) (Banerjee *et al.*, 2002), we observed that the ligand can act as a neutral bridging ligand as well as a bidentate chelating ligand, maintaining its characteristic inner-salt structural features. As part of our ongoing

interest in exploring the versatility of the binding mode of the ligand, we have studied the reactions of the ligand with different oxorhenium(V) starting materials. We report here the structural characterization of a new compound, (II), obtained upon refluxing a chloroform solution of the common oxorhenium(V) starting material [ReOCl₃(PPh₃)₂] with ligand (I).

A perspective view of (II) is shown in Fig. 1, and selected bond lengths and angles are given in Table 1. The structure of (II) can be described as a dimer of the [(Et₂N)₂C₂S₂] unit connected *via* the methylene group at the C21 position, maintaining essentially the same structural features as the [(Et₂N)₂C₂S₂] ligand. The S1—C21—S3 bridging angle is 113.64 (12)°, a significant deviation from the idealized tetrahedral angle, while the two C=S terminal bonds are oriented *trans* to one another, thus minimizing the steric interaction between the ligand halves. The Re—O bond length is 1.6796 (17) Å and lies within the range of normal Re≡O triple-bond values [1.68 (3) Å; Banerjee *et al.*, 2000, and references therein]. The Re—Cl bond lengths lie in the range 2.3896 (6)—2.4550 (5) Å and are within the range of normal values (Gilli *et al.*, 1982; Shivakumar *et al.*, 1998; Banerjee *et al.*, 2000). The Re—Cl3 bond is the longest, as it lies *trans* to the Re≡O triple bond. The geometric parameters for the organic cation are significant, as they define the electronic structure of the ligand. The backbone C9—C10 and C11—12 bonds are longer (~0.02 Å) than that of the free ligand, (I) [1.47 (2) Å; Nagasawa *et al.*, 1995]. The C—N bond lengths are shorter and are close to the normal C=N double-bond length [1.316 (9) Å; Allen *et al.*, 1987]. The N—C—N bond angles [125.4 (2) and 126.5 (2)°] are close to the value for the


Figure 1

A view of (II), with the atom-numbering scheme. Displacement ellipsoids are drawn at the 50% probability level. H atoms have been omitted for clarity.

free ligand [122 (1)°]. The most significant features of (II) are the dihedral angles between the S/C/S and N/C/N planes, *viz.* 104.5 (2)° (S4/C11/S3 and N2/C12/N4) and 104.7 (2)° (S1/C10/S2 and N1/C9/N2), respectively, for the two halves of the ligand. These dihedral angles are significantly larger than that observed in the free ligand [98.0 (1)°; Nagasawa *et al.*, 1995]. There are three different kinds of C—S bond lengths in the compound. The S2—C10 and S4—C11 bonds [1.615 (2) and 1.634 (2) Å, respectively] are close to the C=S double-bond value (Allen *et al.*, 1987) and much shorter than those in the free ligand [1.67 (2)–1.68 (2) Å]. The S1—C10 [1.740 (2) Å] and S3—C11 [1.708 (2) Å] bonds display multiple-bond character. The S1—C21 and S3—C21 bond lengths are 1.800 (2) and 1.801 (2) Å, respectively, and are comparable to the normal C—S single-bond length [1.79–1.82 (1) Å; Miller *et al.*, 2000].

Experimental

To a solution of [ReOCl₃(PPh₃)₂] (0.1 g, 0.12 mmol) in chloroform (15 ml) was added the ligand [(Et₂N)₂C₂S₂] (0.083 mg, 0.36 mmol) (Nakayama & Akiyama, 1992) and the solution was refluxed for 5 h. The resulting dark-brown reaction mixture was subjected to chromatographic separation (MeOH—CH₂Cl₂ 2:98) using a silica-gel column. The light-pink–orange fraction was collected and evaporated under vacuum to give an orange solid (yield: 32 mg, 30%). Analysis found: C 29.95, H 5.24, N 6.58%; C₂₁H₄₂Cl₅N₄OReS₄ requires: C 29.35, H 5.04, N 6.52%. Crystals of (II) suitable for single-crystal X-ray diffraction were grown by slow diffusion of a solution of (II) in CH₂Cl₂ into hexane at room temperature.

Compound (II)

Crystal data

(C ₂₁ H ₄₂ N ₄ S ₄)[ReCl ₅ O]	Mo K α radiation
$M_r = 858.28$	Cell parameters from 11 209 reflections
Monoclinic, $P2_1/n$	$\theta = 1.8\text{--}31.5^\circ$
$a = 13.1381 (5) \text{ \AA}$	$\mu = 4.28 \text{ mm}^{-1}$
$b = 16.3486 (7) \text{ \AA}$	$T = 90 (2) \text{ K}$
$c = 15.7094 (6) \text{ \AA}$	Block, orange
$\beta = 94.003 (1)^\circ$	$0.23 \times 0.16 \times 0.10 \text{ mm}$
$V = 3366.0 (2) \text{ \AA}^3$	
$Z = 4$	
$D_x = 1.694 \text{ Mg m}^{-3}$	

Data collection

Bruker SMART APEX CCD area-detector diffractometer	11 209 independent reflections
φ and ω scans	10 065 reflections with $I > 2\sigma(I)$
Absorption correction: multi-scan (SADABS; Sheldrick, 1996)	$R_{\text{int}} = 0.028$
$T_{\text{min}} = 0.440$, $T_{\text{max}} = 0.674$	$\theta_{\text{max}} = 31.5^\circ$
43 155 measured reflections	$h = -19 \rightarrow 19$
	$k = -24 \rightarrow 23$
	$l = -23 \rightarrow 23$

Refinement

Refinement on F^2	$w = 1/[\sigma^2(F_o^2) + (0.031P)^2 + 2.8947P]$
$R[F^2 > 2\sigma(F^2)] = 0.025$	where $P = (F_o^2 + 2F_c^2)/3$
$wR(F^2) = 0.064$	$(\Delta/\sigma)_{\text{max}} = 0.003$
$S = 1.07$	$\Delta\rho_{\text{max}} = 1.83 \text{ e \AA}^{-3}$
11 209 reflections	$\Delta\rho_{\text{min}} = -0.47 \text{ e \AA}^{-3}$
333 parameters	
H-atom parameters constrained	

Table 1

Selected geometric parameters (Å, °) for (section).

Re1—O1	1.6796 (17)	S3—C11	1.708 (2)
Re1—Cl1	2.3896 (6)	S3—C21	1.801 (2)
Re1—Cl2	2.3998 (6)	S4—C11	1.634 (2)
Re1—Cl5	2.4099 (6)	N1—C9	1.326 (3)
Re1—Cl4	2.4199 (5)	N1—C3	1.488 (3)
Re1—Cl3	2.4550 (5)	N1—C2	1.489 (3)
S1—C10	1.740 (2)	N2—C9	1.337 (3)
S1—C21	1.800 (2)	C9—C10	1.516 (3)
S2—C10	1.615 (2)	C11—C12	1.513 (3)
O1—Re1—Cl1	95.48 (6)	C9—C10—S2	120.08 (16)
O1—Re1—Cl2	94.65 (6)	C9—C10—S1	111.91 (15)
O1—Re1—Cl5	92.96 (6)	S2—C10—S1	128.00 (13)
O1—Re1—Cl4	92.26 (6)	C12—C11—S4	119.22 (16)
O1—Re1—Cl3	175.95 (6)	S4—C11—S3	129.47 (14)
N1—C9—N2	125.4 (2)	N3—C12—N4	126.5 (2)
N1—C9—C10	117.84 (19)	N3—C12—C11	116.6 (2)
N2—C9—C10	116.77 (19)		

All H atoms were located in difference Fourier maps and then allowed for as riding atoms, with $U_{\text{iso}}(\text{H})$ values of $1.2U_{\text{eq}}(\text{parent atom})$. A residual peak of electron density was located in the vicinity of the Re atom. However, the absorption correction could not be adjusted to further minimize this residual. Such residuals are not uncommon in structures containing atoms with large absorption coefficients.

Data collection: SMART (Bruker, 2000); cell refinement: SMART-NT; data reduction: SAINT-NT (Bruker, 2000); program(s) used to solve structure: SHELXTL-NT (Bruker, 2000); program(s) used to refine structure: SHELXTL-NT; molecular graphics: SHELXTL-NT; program used to prepare material for publication: SHELXTL-NT.

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: FG1741). Services for accessing these data are described at the back of the journal.

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