# Ni–Ni Interaction in Di-μ-ethylthiolatobis(ethyltrithiocarbonato)dinickel(II)

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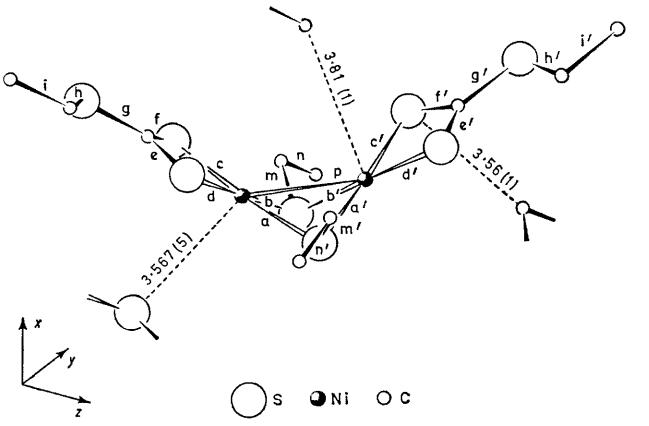
*Summary* An *X*-ray three-dimensional analysis of di-μ-ethylthiolatobis(ethyltrithiocarbonato)dinickel(II) shows the compound to consist of dimers having a wedge-shaped conformation with square planar co-ordination of S around Ni and an intermetallic bond.

IN attempting to crystallize bis(ethyltrithiocarbonato)-nickel(II) from $CHCl_3$–$Et_2O$ by slow evaporation, we obtained a crystalline compound di-μ-ethylthiolatobis-(ethyltrithiocarbonato)dinickel(II) whose molecules have an unusual wedge-shaped conformation, with a Ni · · · Ni interaction. The black crystals were examined using Cu-$K_\alpha$ radiation: $[Ni(CS_3C_2H_5)(SC_2H_5)]_2$, $M.W.$ = 514·2, monoclinic, $a$ = 8·70(1), $b$ = 22·50(1), $c$ = 10·57(1) Å, $\beta$ = 101·2(0·1)°, $V_c$ = 2069 Å$^3$, $D_m$ = 1·63, $Z$ = 4, $D_c$ = 1·65, space group $P\,2_1/c$ (No. 14). The intensities of 1911 independent reflections (4526 possible) were measured photometrically on equi-inclination Weissenberg photographs (Cu-$K_\alpha$). The structure was solved by three-dimensional Patterson and Fourier methods and least-squares anisotropic refinement using all reflections has reduced $R$ to a value of 0·088.

The molecules are dimers formed by two square-planar nickel atoms each surrounded by two sulphur atoms of a trithiocarbonate group and two sulphur atoms of two ethylthiolate groups which form bridges between two metal atoms. The conformation of the molecule is wedge-shaped as the two co-ordination planes form a dihedral angle of 110·2° (Figure). This is a consequence of the predominantly tetrahedral nature of the metal–sulphur bonds formed by the thiolato bridges and by a metal–metal interaction between the two nickel atoms of the dimer: Ni–Ni = 2·76 Å. As far as we know, this is the first example of binuclear planar $Ni^{II}$ complex with Ni–Ni bonds. Dimers with thiolate bridges and a Fe–Fe = 2·61 Å bond have been recently found in di-μ-trithiocarbonatodi-μ-ethylthiolatobis(trithiocarbonato)di-iron(III),[1] but in this compound the dimers are formed by two octahedra sharing an edge.

Packing is mainly determined by two contacts formed by the Ni atoms in the direction of the $d_{z^2}$ orbitals, one with a sulphur atom, Ni · · · S = 3·57 Å, the other with a methyl group, Ni · · · C = 3·81 Å, of two adjacent molecules; one




| | | | |
|---|---|---|---|
| $a$ | 2·179(4) Å | $a'$ | 2·196(3) Å |
| $b$ | 2·184(3) | $b'$ | 2·186(4) |
| $c$ | 2·201(4) | $c'$ | 2·215(3) |
| $d$ | 2·216(3) | $d'$ | 2·211(4) |
| $e$ | 1·67(1) | $e'$ | 1·67(1) |
| $f$ | 1·68(1) | $f'$ | 1·70(1) |
| $g$ | 1·70(1) | $g'$ | 1·71(1) |
| $h$ | 1·78(1) | $h'$ | 1·83(1) |
| $i$ | 1·54(2) | $i'$ | 1·59(2) |
| $m$ | 1·81(1) | $m'$ | 1·81(1) |
| $n$ | 1·51(2) | $n'$ | 1·51(2) |

$p$ = 2·763(2)

| | | | |
|---|---|---|---|
| $ab$ | 81·6(1)° | $a'b'$ | 81·1(1)° |
| $ad$ | 100·8(1) | $a'd'$ | 100·7(1) |
| $bc$ | 98·8(1) | $b'c'$ | 100·0(1) |
| $cd$ | 78·7(1) | $c'd'$ | 78·4(1) |
| $cf$ | 84·0(4) | $c'f'$ | 84·1(4) |
| $de$ | 83·9(4) | $d'e'$ | 85·0(4) |
| $ef$ | 113·4(6) | $e'f'$ | 112·3(7) |
| $eg$ | 126·3(8) | $e'g'$ | 128·3(7) |
| $fg$ | 120·3(7) | $f'g'$ | 119·4(8) |
| $gh$ | 103·0(6) | $g'h'$ | 101·9(6) |
| $hi$ | 108·9(9) | $h'i'$ | 101·9(1·0) |
| $aa'$ | 78·3(1) | $bb'$ | 78·4(1) |
| $am'$ | 113·0(4) | $bm$ | 111·9(4) |
| $a'm'$ | 110·1(5) | $b'm$ | 111·5(4) |
| $m'n'$ | 111·2(1·0) | $mn$ | 111·1(9) |

FIGURE. *Clinographic projection of a molecule of* $[Ni(CS_3C_2H_5)(SC_2H_5)]_2$.

more packing contact concerns a sulphur atom and a methylene group, S · · · C = 3·56 Å.

The calculations were performed on the computers: Elea 6001/*S* of the Centro di Calcolo Elettronico della Università di Parma and C.D.C. 6600 of the Centro di Calcolo Interuniversitario dell'Italia Nord-Orientale (Bologna).

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[1] D. Coucouvanis, S. J. Lippard, and J. A. Zubieta, *J. Amer. Chem. Soc.*, **1969**, **29**, **761**.