Crystal Structure of a Sulphur-rich Nickel(II) Dithiolate $Ni(S_3CC_6H_4Pr^i)(S_2CC_6H_4Pr^i)$

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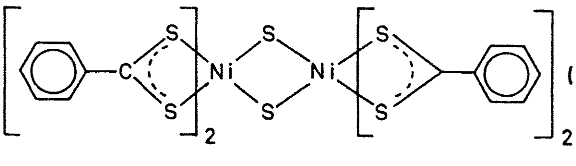
Summary The product prepared by oxidation of nickel(II) dithiocumoate (*p*-isopropylbenzenecarbodithioate) is shown by unequivocal structure determination to contain an oxidized ligand having a S–S linkage.

HIEBER and BRÜCK[1] described the violet complex formed on *oxidizing* nickel(II) dithiobenzoate with sulphur or polysulphides as a dimeric complex of nickel(IV), (1). Physical and chemical evidence led to the reformulation[2–4] of this species as a planar quadratic nickel(II) complex in which one of the chelate rings contains a disulphide linkage (Figure). Similar "sulphur-rich" complexes of nickel have been made from a variety of aryldithio-acids.[3,4] Recently the crystal structure of the iron(III) complex of $Fe(L\text{–}R)_3S$, L–R=*p*-dithiotoluoate, confirmed the existence of the sulphur-rich trithioperoxy-acid ligand.[5] As described here, the nickel(II) complex[4] of trithioperoxycumoato(dithiocumoato)nickel(II), $Ni(L\text{–}R)_2S$, L–R=*p*-dithiocumoate, contains a ligand-*oxidized* chelate ring and four-co-ordinate nickel(II), consistent with the structure proposed by Fackler and Coucouvanis.[2]

Two additional significant features appear in the structure of $Ni(LPr^i)_2$. Except for the isopropyl "tails" and the phenyl group bonded to the sulphur-rich chelate ring, the complex is nearly planar. The 3° Ni–S–S–C torsional angle produced by this planarity is significantly different from the *ca.* 90° X–S–S–X torsional angle generally observed[6] with disulphides as a consequence of S–S lone-pair repulsions. The large dihedral angle observed between the planes of the sulphur-rich chelate ring and its attached phenyl group is also quite striking and suggests a decreased phenyl π-electron interaction in this ligand compared with the dithiocumoate ligand bonded to the same nickel atom.



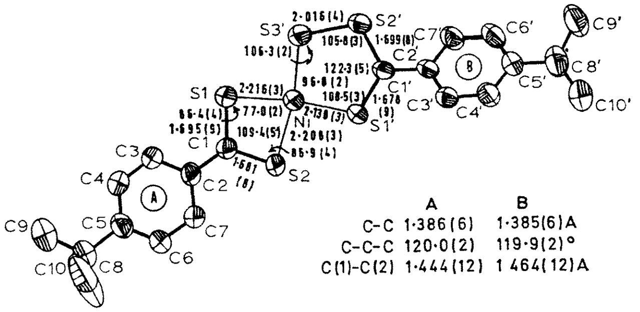
(1)

Crystals of $C_{20}H_{22}NiS_5$ are deep-violet, triclinic plates, $a = 14{\cdot}166(4)$, $b = 13{\cdot}128(4)$, $c = 6{\cdot}408(1)$ Å, $\alpha = 106{\cdot}21(1)°$, $\beta = 85{\cdot}78(1)°$, $\gamma = 108{\cdot}82(1)°$, $V_c = 1084$ Å^3, $D_m = 1{\cdot}463$ g cm^{-3}, $Z = 2$, $D_c = 1{\cdot}468$ g cm^{-3}, space group $P\bar{1}$. A total of 2776 independent data were collected on a Picker four-circle diffractometer using Cu-K_α radiation. The data were corrected for absorption. The structure was solved by the heavy-atom method and refined by full-matrix, anisotropic (hydrogen atoms isotropic), least-squares to a final R value of 0·061. Anomalous dispersion corrections,[7] real and imaginary terms, were applied to the nickel and sulphur atomic form-factors.[8,9]

The molecule is illustrated in the thermal ellipsoid plot which presents selected bond distances and angles. The mean Ni–S distance was significantly shorter for the trithioperoxy-acid ligand compared with the dithio-acid ligand as in iron(III) complex.[5] No "*trans*-effect" was observed, *i.e.* the Ni–S bonds were structurally equivalent in each ligand. The S–S bond[6] is shorter (by *ca.* 0·07 Å) than that found[5] in Fe(L–Me)$_2$S.

The least-squares plane calculated through the nickel atom and the four sulphur atoms co-ordinated to it shows a r.m.s. deviation for the five atoms of 0·041 Å. The trithioperoxycumoate chelate ring is planar with an r.m.s. deviation of 0·018 Å. Consequently, we do not observe the puckering previously reported in the iron complex.[5]

The phenyl ring associated with the dithiocumoate ligand (A) is tilted 8° from the plane of the four-membered chelate ring while the trithioperoxycumoate ring (B) is tilted by 143° from its associated chelate ring. These differences in co-planarity of rings are undoubtedly attributable to 1,4-non-bonded intramolecular contacts between phenyl hydrogens and the chelate ring sulphur atoms. The S · · · H distances are constant at 2·7 ± 0·1 Å. This distance necessitates a displacement of the phenyl group out of the plane of the five-membered chelate ring because of the opened S–C–S angle. A spectral consequence would be a shift of the lowest energy π–π^* transition to higher energy. Structurally it seems unlikely that either phenyl group in NiL_2S_2 complexes will be found co-planar with its associated chelate ring. The spectral shifts observed[3] for NiL_2, NiL_2S, and †NiL_2S_2 are consistent with this possibility.



	A	B
C-C	1·386(6)	1·385(6)A
C-C-C	120·0(2)	119·9(2)°
C(1)-C(2)	1·444(12)	1 464(12)A

Unlike the situation for[10] Ni(L–H)$_2$, the Ni(L–Pr^i)$_2$S complex exists as a discrete monomolecular unit, the molecules being "stacked" in a staggered array. There are no shorter contacts than 3·61 Å, a sulphur–sulphur interaction.

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† *Added in proof:* The X-ray crystal structure of ZnL_2S_2 shows two trithioperoxycumoato ligands with an excellent tetrahedral geometry about zinc.

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