The Geometry of the Bis(trithiocarbonate)nickel(II) Anion, [Ni(CS$_3$)$^{2-}$]

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RECENT chemical[1,2] and crystallographic[3-7] interest in complexes of nickel with molecules which contain two sulphur atoms and which are capable of acting as bidentate ligands, has prompted us to examine the geometry of the bistrithiocarbonatenickel(II) anion (I), by means of a single-crystal *X*-ray analysis on the tetraphenylarsonium salt, $[Ph_4As]_2^+[Ni^{II}(CS_3)_2]^{2-}$.

The following cell data were obtained from precession photographs with Mo-K_α radiation (λ = 0·7107 Å): $C_{50}H_{40}AsS_6Ni$, M = 1041·8, *monoclinic*, a = 26·45 ± 0·03, b = 9·57 ± 0·02, c = 19·80 ± 0·03 Å β = 112°45′ ± 15′, V = 4622·5 × 10^{-24} cm.^{3}, ρ_m = 1·49 g. cm.$^{-3}$, Z = 4, ρ_c = 1·50 g. cm.$^{-3}$. The possible space groups are $C2/c$ or Cc; the former is established by the results of the analysis, with the bistrithiocarbonatenickel(II) anion positioned on a two-fold axis through the nickel atom, and relating one trithiocarbonate ligand to the other. After two cycles of full-matrix least-squares refinement with anisotropic temperature factors, the R-factor on 1951 independent, non-zero reflexions, collected on equi-inclination Weissenberg photographs with Cu-K_α radiation is 0·11. The dimensions of the bistrithiocarbonatenickel(II) anion are shown in the Figure.

The structure of the ion closely resembles those found for bisdithiocarbamatenickel(II) complexes (II)[3,4] and bisxanthatenickel(II) complexes (III),[5] where the respective C–N and C–O lengths indicate a substantial degree of double-bond character. We find that the C–S lengths in (I) imply substantial multiple-bond character in all C–S bonds including the exocyclic one.

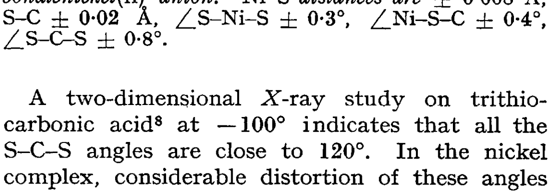
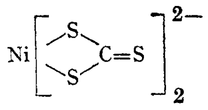
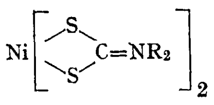


FIGURE. *Bond lengths and angles in the bistrithiocarbonatenickel*(II) *anion.* Ni–S *distances are* ± 0·008 Å, S–C ± 0·02 Å, ∠S–Ni–S ± 0·3°, ∠Ni–S–C ± 0·4°, ∠S–C–S ± 0·8°.

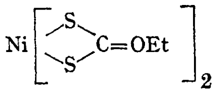
A two-dimensional *X*-ray study on trithiocarbonic acid[8] at −100° indicates that all the S–C–S angles are close to 120°. In the nickel complex, considerable distortion of these angles occurs with the endocyclic S–C–S angle being reduced to 107·3°, which is significantly smaller than the values found for the corresponding angle in the dithiocarbamate (111°) and xanthate (116°) complexes.[3-5] A high degree of overlap of sulphur



(I)



(II) a; R=Et
b; R=H



(III)

orbitals with the dsp^2 orbitals of the $\mathrm{Ni^{II}}$ is preserved by a compensating increase in the C–S–Ni angles (88°) when compared to the dithiocarbamate (85°) and xanthate (82°) complexes. In all four examples involving a four-membered chelate ring,[3-5] the sum of the internal valency angles is almost exactly 360°. In the unsubstituted bisdithiocarbamatenickel(II) complex (IIb),[4] a significant deviation from planarity of the nickel and four sulphur atoms is reported, but not described. We find that, whereas the nickel, carbon, and two sulphur atoms of the one ligand are coplanar within the accuracy of the analysis, the nickel and four co-ordinated sulphur atoms are nonplanar. This deviation can be described as a tetrahedral buckling, with the plane through the atoms S(1), Ni, and S(2) making an angle of 5° with the plane through the atoms S(1′), Ni, and S(2′).

There appears to be a definite correlation between increase of the Ni–S distance with the decrease in Ni–S–C angle in the series of bisdithionickel complexes. The values range from the Ni–S distance of 2·146 Å and Ni–S–C angle of 103·3° found in bis-1,2-dicyanoethylene-1,2-dithiolatonickel(III)[6] to the distance of 2·23 Å and angle of 82° found in the bisxanthatenickel(II) complex.[5] The values found in the present investigation support such a correlation.

The overall difference in charge between the present species and the dithiocarbamate and xanthate structures is unlikely to affect the ligands to a significant extent, judging by the results of a comparison between $\{\mathrm{Ni[S_2C_2(CN)_2]_2}\}^{2-}$ and $\{\mathrm{Ni[S_2C_2(CN)_2]_2}\}^{-}$,[6,7] where it is thought that the additional electron in the latter ion is located primarily on the nickel atom.

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