SHORT COMMUNICATIONS

Is There Evidence for Non-linear Thiocyanate or Selenocyanate Ions?

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Abstract

The structure of a mixed-valence copper complex with 1,10-phenanthroline, $[Cu^{II}(phen)_2]$–NC–$[Cu^{I}(phen)((Se,S)CN)]$-$[(Se,S)CN].0.5(C_2H_5OH)$, μ-cyano-$1\kappa N:2\kappa C$-(seleno,thio)-cyanato-$2\kappa N$-tris(1,10-phenanthroline)-$1\kappa^4 N,N';2\kappa^2 N,N'$-dicopper(I,II) (seleno,thio)cyanate semiethanolate, has been revised from space group Cc to $C2/c$. Refinement in $C2/c$ has shown that, contrary to the Cc results, the (Se,S)CN anions can be described as approximately linear, as expected.

1. Introduction

The crystal structure of this compound was originally described (Dunaj-Jurčo *et al.*, 1993; DKKCM) in space group Cc, with two complex Cu^{II}–Cu^{I} cations and two (Se,S)CN anions in the asymmetric unit. Both anions showed two distinct types of disorder: substitutional disorder at the (Se,S) site and positional disorder of the N atom; as a result of this latter disorder, four different conformations were reported. One conformation was, as usual, approximately linear [angle at the central C atom, 175.8 (12)°]. However, in the other three arrangements the ion was appreciably bent, with the central angle ranging from 140.3 (10) to 152.5 (15)°. As far as I am aware, there is no other solid-state structure in which either the SeCN or the SCN anion has been shown to be other than approximately linear. [From a search of the October 1997 release of the Cambridge Structural Database (1992) I found 44 entries containing 71 examples of either coordinated or uncoordinated Se−C−N groupings; among the reliable examples, the smallest angle at the C atom was 175°.† The average bond lengths were Se−C 1.80 (5) and C−N 1.15 (3) Å. I have not critically surveyed the thiocyanate entries, which number over 1000.]

DKKCM also noted that the two independent cations 'are nearly centrosymmetrically related', suggesting that the actual space group might be $C2/c$ rather than Cc; if this were the case, refinement of the centrosymmetric structure in the non-centrosymmetric space group Cc might well have led to distortions in the structure and to non-linear anions. Accord-

ingly, I have re-refined the structure in $C2/c$ and have demonstrated that there is no reason to describe the anions as other than approximately linear.
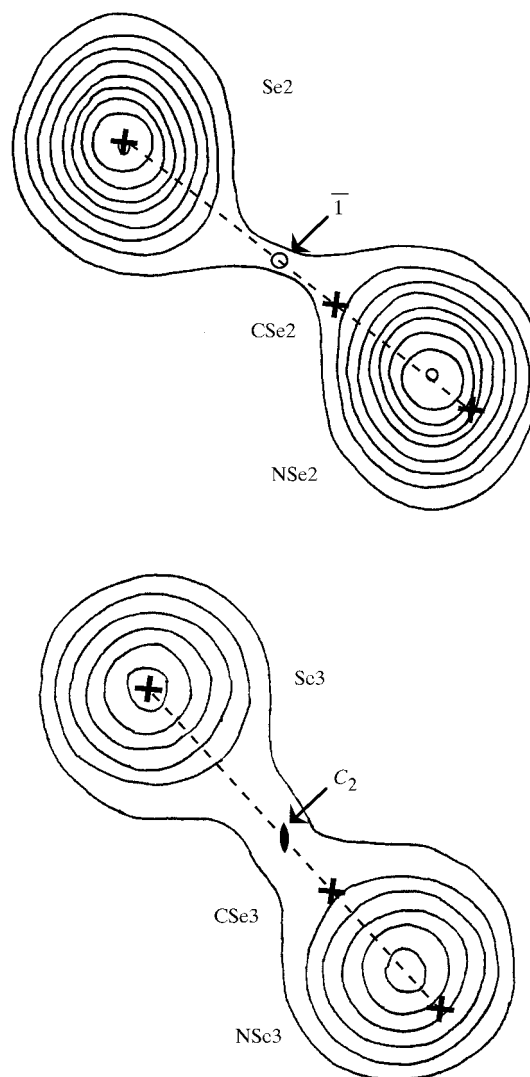

Fig. 1. Electron density maps in the planes of the two anions. Besides the occupancy disorder at the Se sites (which are a mixture of Se and S), both anions are disordered across the indicated symmetry elements. Final positions are indicated by crosses, those of the C and N atoms having been fixed so as to give linear (Se,S)−C−N groups with distances (Se,S)−C 1.76 and C−N 1.14 Å.

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† For one of the six SeCN ions in TULLAN (refcode), the calculated angle is 163°; however, this structure is closely centrosymmetric and the reported space group $P1$ is probably incorrect. When the coordinates are averaged according to space group $P\bar{1}$, the smallest angle becomes 177°. The angle in WADVOM is reported as 143 (18)°, the very large e.s.d. being due to a poor crystal and the small number of data; R was relatively large, 0.08. Of the two entries leading to angles of 172°, one (SECBNZ) carries a large e.s.d., 3°, and the other (SUDNAG) had problems with misprinted coordinates in the original paper.

In *C2/c*, as in *Cc*, there are two independent (Se,S)CN anions, occupationally disordered at the Se,S site and also positionally disordered; one [Se(2)—C(Se2)—N(Se2)] is disordered across a centre of symmetry and the other [Se(3)—C(Se3)—N(Se3)] is disordered across a twofold axis. Electron density maps for these two groups, calculated after final refinement in *C2/c*, are shown in Fig. 1. While various interpretations of these maps are possible, none suggest that the ions are other than linear. The final models I have chosen are shown in Fig. 1, with the anions constrained to be linear and to lie exactly on a symmetry element ($\bar{1}$ or C_2). The Se—C and C—N distances were fixed (1.76 and 1.14 Å). Anisotropic *U*'s for the combined Se,S atoms were refined, as were the relative occupancy factors (x for Se, $1 - x$ for S); isotropic *U*'s for the C and N atoms were set equal to the U_{eq}'s of the (Se,S) atoms.

The solvent molecule, presumed to be C_2H_5OH, must also be disordered around a C_2 axis in *C2/c*. I have chosen to model it with only two isotropic atoms: a fully occupied site for the C atom and a half-occupied O site. While the resulting geometry is not outlandish [C—C 1.40 (5), C—O 1.36 (6) Å, C—C—O 94 (3)°], an electron density map shows that this model is an oversimplification, in that the C_2 axis obviously does not lie at the center of the C—C bond.

2. Experimental

My refinement in *C2/c* began with the coordinates and *U*'s reported in the earlier paper (DKKCM), appropriately symmetrized and averaged; F_{obs} values were from the supplementary data of the previous paper (SUP 71075). The final full-matrix least-squares refinement was based on 1964 'observed' reflections and 382 parameters, including distribution parameters for the three Se,S sites, and anisotropic U^{ij}'s for Cu and Se(S), and for the outer C atoms of the phenanthroline rings (which showed large librations); the anions were constrained as described earlier. Hydrogen parameters were assigned. At convergence the maximum shift was 0.07σ; the largest features on a difference map were two peaks of 0.7 e Å^{-3}, near Se(2) and Se(3). The final *R* was 0.066, compared with *R* 0.065 reported by DKKCM for 1948 reflections and 469 parameters.

The three (Se,S)CN groups seemingly show different amounts of substitutional disorder between Se and S, the amount of Se being 0.69 (1) at the coordinated Se(1) site, 0.60 (2) at Se(2) and 0.52 (3) at Se(3); however, the latter two values are undoubtedly more uncertain than their formal e.s.d.'s, because of uncertainties as to how the positional disorder should be modelled. Bond lengths and angles within the cation are generally normal, except for some peripheral C—C bonds which range down to 1.24 (4) Å; this shortening is presumably due to the librations noted earlier. Some of these bond lengths were even shorter in the earlier *Cc* refinement; other C—C distances were improbably long (over 1.5 Å). Other aspects of the structure reported by DKKCM are confirmed by the present refinement, including a significant difference between the axial [2.02 (1) Å] and equatorial [2.07 (1) Å] Cu^{II}—N bonds and distorted tetrahedral coordination about the Cu^I atom.

References

Cambridge Structural Database (1992). Version 4.6. Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge, England.

Dunaj-Jurčo, M., Kabešová, M., Kettmann, V., Cisařová, I. & Mikloš, D. (1993). *Acta Cryst.* C**49**, 1476–1479.