The Structure, Geometry, and Bonding in $Co[SC(NH_2)_2]_4(NO_3)_2$ and $Co[SC(NH_2)_2]_4(NO_3)_2{\cdot}H_2O$

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Summary The structure, geometry, and bonding in $Co[SC(NH_2)_2]_4(NO_3)_2$ and $Co[SC(NH_2)_2]_4(NO_3)_2{\cdot}H_2O$ are reported: it is shown that the transition metal is bonded to thiourea through the ligand π-molecular orbital.

IT has been demonstrated that tetrahedral or octahedral stereochemistry of Co^{II} can usually be established from the visible spectra of the complex in solution and the magnetic susceptibility.[1,2] However, the interpretation of these measurements for tetrakis(thiourea)cobalt(II) nitrate [$Cotu_4(NO_3)_2$] by Cotton *et al.*,[3] led to an ambiguous assignment of stereochemistry. These authors suggested octahedral Co^{II}, whereas Adams and Cornell[4] concluded that both $Cotu_4(NO_3)_2$ and $Cotu_4(ClO_4)_2$ were tetrahedral based on their far i.r. spectral measurements. We investigated the crystal structure of $Cotu_4(NO_3)_2$ as the monohydrate and as the anhydrous material.† The water of hydration does not effect the Co^{II} stereochemistry.

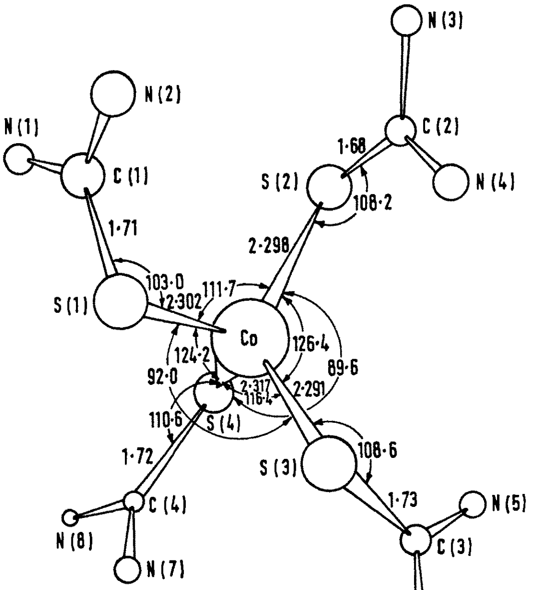

FIGURE 1. *A perspective view of the* $Co(thiourea)_4{}^{2+}$ *molecular ion showing the principal bonded distances and angles. Maximum e.s.d.'s from full-matrix least-squares refinement are*: Co–S ± 0·004, S–C ± 0·013, C–N ± 0·016 Å, S–Co–S ± 0·1, Co–S–C ± 0·4, *and* N–C–N ± 1°. *The* C–N *distances are not significantly different from the* 1·32 Å *average and the* C–N–C *angles are not significantly different from* 120°.

$Cotu_4(NO_3)_2{\cdot}H_2O$(I) and $Cotu_4(NO_3)_2$(II) both crystallize in the orthorhombic space group *Pbcm*. For (I): $a =$ 33·704(8), $b =$ 11·734(2), $c =$ 10·253(2) Å, $U =$ 4055 Å^3, $M =$ 501, $D_m =$ 1·68(2), $D_c =$ 1·66 g cm^{-3}, $Z =$ 8($\lambda =$ 0·71068 Å); for (II): $a =$ 35·88(2), $b =$ 11·35(4), $c =$ 9·30(2) Å, $U =$ 3787 Å^3, $M =$ 483, $D_m =$ 1·68(2), $D_c =$ 1·69 g cm^{-3}, and $Z =$ 8($\lambda =$ 1·1903 Å). For (I) the intensities of 1815 independent non-zero reflections were recorded with a Picker automatic diffractometer with Mo-K_α radiation ($\lambda =$ 0·71068 Å). For (II) the intensities of 780 independent non-zero reflections were measured by standard equi-inclination multiple-film Weissenberg photographic techniques. The crystal structures were solved by conventional heavy-atom techniques and refined by full-matrix least-squares. (I) and (II) refined to a conventional *R* of 0·066 and 0·156, respectively.

The crystal structures of (I) and (II) may be described as made up of $Cotu_4{}^{2+}$ and $NO_3{}^-$ ions held together by ionic and van der Waals interactions as well as hydrogen bonds. In the hydrate structure, the water functions as a binding agent for the nitrate ions. The configuration of the $Co(tu)_4{}^{2+}$ molecular ion (Figure 1) may be specified (considering only the Co and its four nearest sulphur neighbours) as only very approximately tetrahedral with a distortion produced by compression along one of the tetrahedral S_4 axes and a corresponding slight twist of the tetrahedral apices (occupied by S atoms) related by this axis in opposite directions. This distortion gives the CoS_4 unit approximately C_2 symmetry. Therefore, the stereochemistry about Co in $Co(tu)_4{}^{2+}$ is best described as distorted tetrahedral, more or less, in agreement with the interpretation of the far i.r. spectral measurements of Adams and Cornell, but at variance with the interpretation of the visible and u.v. spectra as well as the magnetic measurements.[3] These distortions can be seen from the S–Co–S angles in Figure 1. The average Co–S distance of 2·304 Å is significantly shorter than the 2·502(6) and 2·553(6) Å Co–S distances observed in *trans*-$Co(tu)_4Cl_2$,[5] but longer than the Co–S distances of 2·144(6) to 2·245(6) Å found in $[SCo_3(CO)_7]S_2$,[6] and the average 2·162(6) Å observed in $\{[(CF_3)_2C_2S_2]_2Co\}_2$.[7] The fact that our values for the Co–S bond lengths are between these two is to be expected. There is probably little of the usual type of Co–S π-bonding in

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† The monohydrate was investigated by E. L. A., the anhydrous material by P.S.G.

trans-Co(tu)$_4$Cl$_2$, but a good deal in the planar $(R_2C_2S_2)_2Co$ systems. Some Co–S π-bonding is expected in a tetrahedral CoS$_4$ fragment since the σ- and π-orbitals are no longer orthogonal. The orientation of the thiourea groups containing S(2), S(3), and S(4) may be seen from the Co–S–C angles as well as the dihedral angles between planes defined by Co–S–C and S–C–N$_2$ [33(1), 34(1), and 25(1)°], respectively.

These angles and dihedral angles fall into the range found for a number of transition metal–thiourea complexes in which sulphur uses an sp^2-orbital for bond formation.[5,8–14] However, the orientation of the S(1) thiourea group in Co(tu)$_4^{2+}$ is vastly different from the other three and from those found in other transition metal–thiourea complexes studied so far.

The Co–S(1)–C(1) angle is significantly smaller than the other Co–S–C angles, and the dihedral angle between planes defined by Co–S(1)–C(1) and S(1)–C(1)–N(1)–N(2) of 75·8(9)° (Figure 2) indicates that this Co–thiourea interaction cannot be using the sulphur sp^2-orbitals for bond formation. The only orbital which is in position for overlap is the thiourea delocalized π-molecular orbital. We believe this is the first example of a transition metal bonding to thiourea through the ligand π-molecular orbital. Bridge bonds utilizing this π-orbital have been observed in the post-transition metal–thiourea complexes, Cu(tu)$_2$Cl,[15] Cu$_4$(tu)$_9$(NO$_3$)$_4$,[16] and Ag(tu)$_2$Cl.[17] Bonding of this type might be expected to elongate the C–S and C–N distances, but nitrogen atoms have sufficient otherwise non-bonding π-electrons to compensate for such loss.

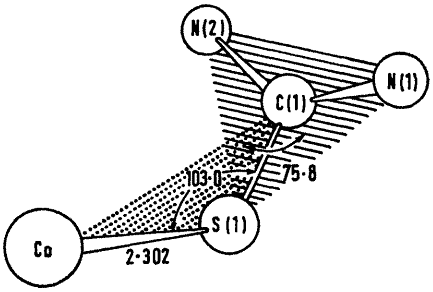

FIGURE 2. *A view of the* S(1) *thiourea group. The distance and angles given completely specify the orientation of this thiourea group relative to the* Co *atom.*

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[1] F. A. Cotton, D. M. L. Goodgame, M. Goodgame, and A. Sacco, *J. Amer. Chem. Soc.*, 1961, **83**, 4157.
[2] F. A. Cotton, D. M. L. Goodgame, M. Goodgame, and T. E. Haas, *Inorg. Chem.*, 1962, **1**, 565.
[3] F. A. Cotton, O. D. Faut, and J. T. Mague, *Inorg. Chem.*, 1964, **3**, 17.
[4] D. M. Adams and J. B. Cornell, *J. Chem. Soc.* (*A*), 1967, 884.
[5] J. E. O'Connor and E. L. Amma, *Chem. Comm.*, 1968, 892.
[6] D. L. Stevenson, V. R. Magnuson, and L. F. Dahl, *J. Amer. Chem. Soc.*, 1967, **89**, 3727.
[7] J. H. Enemark and W. N. Lipscomb, *Inorg. Chem.*, 1965, **4**, 1729.
[8] A. Lopez-Castro and M. R. Truter, *J. Chem. Soc.*, 1963, 1309.
[9] L. Cavalca, M. Nardelli, and A. Braibanti, *Gazzetta*, 1956, **86**, 942.
[10] D. A. Berta, W. A. Spofford, tert., P. Boldrini, and E. L. Amma, *Inorg. Chem.*, in the press.
[11] L. Capacchi, G. F. Gasparri, M. Nardelli, and G. Pelizzi, *Acta Cryst.*, 1968, **24**, *A*, 1199.
[12] S. Ooi, T. Kawase, K. Nakatsu, and H. Kuroya, *Bull. Chem. Soc. Japan*, 1960, **33**, 861.
[13] G. F. Gasparri, A. Mangia, A. Musatti, and M. Nardelli, *Acta Cryst.*, 1969, **25**, *A*, 203.
[14] M. Nardelli, G. F. Gasparri, G. G. Battistini, and P. Domiano, *Acta Cryst.*, 1966, **20**, 349.
[15] W. A. Spofford, tert., and E. L. Amma, *Chem. Comm.*, 1968, 405.
[16] R. G. Vranka and E. L. Amma, *J. Amer. Chem. Soc.*, 1966, **88**, 4270.
[17] (a) E. A. Vizzini and E. L. Amma, *J. Amer. Chem. Soc.*, 1966, **88**, 2872; (b) E. A. Vizzini, I. F. Taylor, jun., and E. L. Amma, *Inorg. Chem.*, 1968, **7**, 1351.