The Molecular Structure of *trans*-Dichlorotetrakisthioureacobalt(II)

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THE controversy over the structure of $Nitu_4Cl_2$[1,2] [tu = $SC(NH_2)_2$] has prompted an *X*-ray study of the analogous cobalt compound. $Cotu_4Cl_2$ is reported to be isostructural with $Nitu_4Cl_2$[1] and interpretation of further experimental work has been based on this report.[3,4] A three-dimensional *X*-ray diffraction study of $Cotu_4Cl_2$ shows that it is *not* isostructural with either of the structures reported for $Nitu_4Cl_2$.

$Cotu_4Cl_2$ crystallizes in the tetragonal space group $P4_2/n$ with $a = 13{\cdot}508 \pm 0{\cdot}007$, $c = 9{\cdot}106 \pm 0{\cdot}005$ Å, $U = 1673$ Å^3, $M = 434{\cdot}2$, $D_m = 1{\cdot}72$, and $D_c = 1{\cdot}72$ for $Z = 4$. Intensities of 885 independent non-zero reflections were recorded with a Picker automated diffractometer using Zr-filtered Mo-K_α radiation ($\lambda = 0{\cdot}71068$ Å). The crystal structure was solved by the conventional Patterson and Fourier methods and refined by full matrix least-squares. All atoms, including hydrogens, have been located. By using anisotropic temperature factors for non-hydrogen atoms and isotropic temperature factors for hydrogen atoms the structure has been refined to a conventional *R* of 0·045.

The $Cotu_4Cl_2$ structure consists of discrete molecules inter-connected with hydrogen bonds; each chlorine is weakly bonded to six hydrogen atoms. The molecular configuration of an isolated unit of $Cotu_4Cl_2$ is shown in the Figure.

The cobalt atom in $Cotu_4Cl_2$ is located on a centre of symmetry and is octahedrally co-ordinated to four sulphur and two chlorine atoms. In contrast to this structure, the nickel atom was first reported to be on a position of $\bar{4}(S_4)$ symmetry with the thiourea ligands alternately tipped up and down.[1] In the second structural determination the metal atom was reported to lie on a position of $4(C_4)$ symmetry with all thiourea ligands tipped in the same direction, toward the shorter of the two Ni–Cl distances (2·40 and 2·52 both $\pm 0{\cdot}02$ Å).[2] Thus the arrangement of ligands and co-ordination geometry of $Cotu_4Cl_2$ are different from either of the two structures reported for $Nitu_4Cl_2$.

The metal-thiourea complexes Mtu_4Cl_2 (M = Mn, Fe, Co, Ni) were reported to be isostructural[1] but this is definitely not the case. Our results indicate that the iron and cobalt complexes are indeed isostructural but they differ significantly from the structure of the nickel analogue. Attempts to isolate single crystals of the manganese complex have so far been unsuccessful. In other metal–thiourea complexes of this type (*e.g.* $Pttu_4Cl_2$ and $Pdtu_4Cl_2$) the metal atoms lie on a crystallographic centre of symmetry.[5,6]

In $Cotu_4Cl_2$ the two independent cobalt–sulphur bond lengths (2·502 and 2·553 both $\pm 0{\cdot}006$ Å) are relatively long compared to the expected value of 2·36 Å, based on the sum of their covalent radii.[7] The cobalt–chlorine bond length of $2{\cdot}469 \pm 0{\cdot}002$ Å is also longer than that expected from the sum of their covalent radii (2·31 Å).[7] It is of interest to note that the Co–Cl distance is almost half-way between the two Ni–Cl distances observed in one

of the structures reported for the analogous $Nitu_4Cl_2$.[2] The average sulphur–carbon distance of 1·72 Å (range: 1·71—1·73 ± 0·01 Å) and the carbon–nitrogen distance of 1·31 Å (range: 1·29—1·33 ± 0·02 Å) agree well with similar values reported for other metal–thiourea complexes[1,2,5,6,8] as well as the distances in thiourea itself.[9,10] The average nitrogen–hydrogen distance of 1·07 Å (range: 1·03—1·11 ± 0·2 Å) is consistent with the values of 1·022 and 1·012 Å reported in the neutron diffraction study of thiourea.[10] Least-squares plane calculations have shown that both thiourea ligands, including hydrogens, are planar within the experimental error. This is also true of the free thiourea molecule.[10]

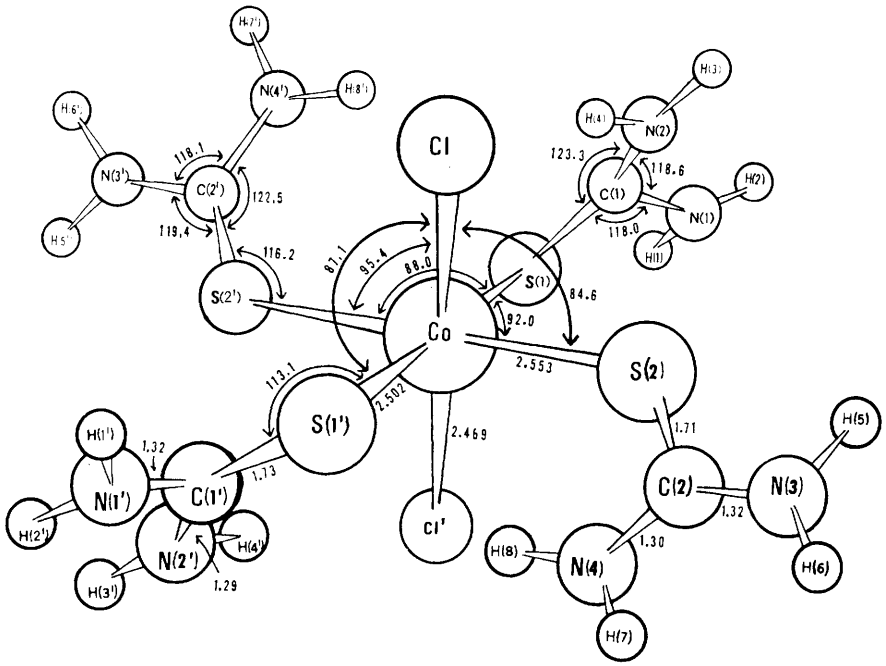

FIGURE. *A perspective view of the molecular configuration of* $Cotu_4Cl_2$. *The cobalt atom lies on a centre of symmetry and only independent distances and angles are indicated*

It is interesting to note that the absorption spectra of $Cotu_4Cl_2$ in anhydrous acetone indicate a tetrahedral co-ordination geometry[11] for Co^{II}.

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