Structural Studies of Metal Complexes with *NN'*-Disubstituted Thioureas. Part II.[1] Crystal Structure of Dichlorobis-(*NN'*-diethylthiourea)cobalt-(II) (Triclinic Form)

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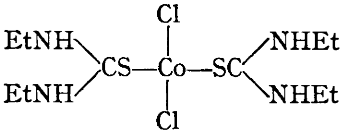
The crystal structure of the title compound has been determined by the heavy-atom method and refined by anisotropic least-squares methods to R 0·101 for 1303 visually estimated independent reflections. Crystals are triclinic, space group $P\bar{1}$, with $Z = 2$, in a unit cell of dimensions: $a = 8{\cdot}931$, $b = 9{\cdot}082$, $c = 15{\cdot}024$ Å, $\alpha = 64°\ 24'$, $\beta = 119°\ 56'$, $\gamma = 111°\ 24'$. The structure consists of polymeric chains of molecules connected to each other by hydrogen bonds between the chlorine and NH groups. The cobalt is tetrahedrally co-ordinated: mean Co–S 2·323, and Co–Cl 2·254 Å.

THE first paper[1] of this series gave the general reasons for the investigation of the structure of metal *NN'*-disubstituted thioureas. Dichlorobis(diethylthiourea)-cobalt(II), [Co(detu)$_2$Cl$_2$], (I), was then studied and two modifications were identified: a monoclinic and a triclinic form. The monoclinic form[1] was found to be isomorphous with Zn(detu)$_2$Cl$_2$. We have therefore undertaken the *X*-ray analysis of the triclinic form of Co(detu)$_2$Cl$_2$.



(I)

EXPERIMENTAL

Crystals were prepared as described in ref. 2. Single blue prismatic crystals suitable for *X*-ray diffraction analysis were

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[1] Part I, M. Bonamico, G. Dessy, V. Fares, and L. Scaramuzza, *J. Chem. Soc.* (*A*), 1971, 3195.

grown by slow evaporation from acetone which also gave the monoclinic form.

TABLE 1

Co-ordinates ($\times 10^4$) and temperature factors * with standard deviations in parentheses

	x/a	y/b	z/c	b_{11}	b_{12}	b_{13}	b_{22}	b_{23}	b_{33}
Co	3606(3)	17(3)	2065(2)	153(5)	90(7)	73(5)	61(4)	−5(5)	48(3)
Cl(1)	6453(5)	−280(6)	2968(4)	218(9)	255(15)	78(9)	265(10)	−61(10)	57(5)
Cl(2)	3484(6)	2736(4)	1290(4)	301(11)	134(12)	162(10)	91(6)	−6(8)	81(5)
S(1)	2025(6)	−1608(4)	929(4)	281(11)	21(12)	146(10)	73(6)	−23(8)	66(4)
S(2)	2155(6)	−1289(5)	3223(4)	267(11)	−24(13)	181(11)	116(7)	−61(9)	92(5)
N(1)	2529(17)	1166(14)	−589(10)	234(30)	155(38)	127(29)	104(24)	10(26)	48(12)
N(2)	3182(16)	1641(13)	3574(11)	190(27)	132(38)	80(28)	88(23)	−24(26)	68(13)
N(3)	2642(18)	−1161(14)	−800(11)	301(35)	96(41)	161(34)	87(22)	−68(27)	70(15)
N(4)	2558(17)	−639(15)	4948(11)	234(30)	155(41)	110(29)	145(25)	12(28)	35(12)
C(1)	2433(17)	−483(15)	−229(11)	161(30)	32(38)	83(30)	65(26)	32(26)	22(14)
C(2)	2679(16)	10(17)	3987(13)	90(26)	146(41)	48(31)	149(31)	−74(34)	57(16)
C(3)	2811(25)	2231(18)	−1598(13)	355(49)	235(56)	116(42)	94(27)	63(32)	43(16)
C(4)	2500(30)	3979(21)	−1892(20)	403(60)	187(66)	198(61)	90(30)	20(43)	155(25)
C(5)	2546(25)	−2976(19)	−444(18)	302(47)	109(55)	164(51)	82(28)	−103(40)	147(23)
C(6)	681(26)	−3688(26)	−1225(22)	197(43)	−37(66)	39(54)	233(44)	−259(60)	189(29)
C(7)	3571(23)	2786(19)	4159(14)	293(43)	131(53)	174(42)	124(30)	−4(35)	67(18)
C(8)	3981(29)	4593(21)	3448(17)	378(55)	178(63)	167(53)	121(32)	−23(40)	109(21)
C(9)	1995(22)	−2398(20)	5399(15)	236(40)	162(55)	190(42)	160(33)	45(37)	79(18)
C(10)	192(27)	−2745(30)	5259(23)	185(44)	223(77)	184(59)	313(54)	152(65)	196(31)

* Exponential coefficients b_{ij} as given here are defined by $T = \exp[10^{-4}(b_{11}h^2 + b_{22}k^2 + b_{33}l^2 + b_{12}hk + b_{13}hl + b_{23}kl)]$.

Crystal Data.—$C_{10}H_{24}Cl_2CoN_4S_2$, $M = 394{\cdot}29$, triclinic, $a = 8{\cdot}931 \pm 0{\cdot}005$, $b = 9{\cdot}082 \pm 0{\cdot}005$, $c = 15{\cdot}024 \pm 0{\cdot}01$ Å, $\alpha = 64° 24' \pm 10'$, $\beta = 119° 56' \pm 10'$, $\gamma = 111° 24' \pm 10'$, $U = 935$ Å^3, $D_m = 1{\cdot}40 \pm 0{\cdot}02$ g cm^{-3} (by flotation), $Z = 2$, $D_c = 1{\cdot}401$ g cm^{-3}, $F(000) = 407{\cdot}54$. Fe-K_α radiation, $\lambda = 1{\cdot}9374$ Å, $\mu(\text{Fe-}K_\alpha) = 114$ cm^{-1}. Space group $P\bar{1}$ (C_i^1, No. 2) from morphology and structure determination. The unit-cell dimensions were determined by an improved version of Christ's method [3] from zero-layer Weissenberg film taken about the c axis, mainly using reflections from Fe-K_{α_1} radiation ($\lambda = 1{\cdot}93604$ Å), and from precession photographs.

Intensity Measurements.—Intensities were estimated visually from sets of multiple-film equi-inclination Weissenberg photographs taken about the c axis (10 layers, $hk0$—9), from an elongated prismatic crystal, *ca.* $0{\cdot}03 \times 0{\cdot}04$ cm. The intensities of 1373 reflections gave a set of 1303 independent reflections above background (*ca.* 51% of those possible with Fe-K_α radiation).

Data Reduction.—Intensity data were corrected for Lorentz and polarization effects, and for spot extension.[4] No absorption or extinction corrections were applied. The first scaling of observed structure amplitudes was based on the relative exposure-times of the different photographs. Independent layer-scales were refined during the isotropic phase of the structure refinement.

Structure Determination.—The structure was solved by the heavy-atom method which led to the location of all atoms except hydrogen. The non-hydrogen atomic positional and isotropic thermal parameters ($\bar{B} = 4{\cdot}0$ Å^2 by Wilson's method), were refined by several cycles of 4×4 block-diagonal least-squares to R 0·145. A new scaling (see earlier) and the introduction of anisotropic thermal motion for all non-hydrogen atoms brought R to 0·101 in nine cycles. Refinement was performed by use of anisotropic thermal parameters with 9×9 block-diagonal approximation; the final shifts on the atomic parameters were all $< 0{\cdot}2\sigma$. The weighting scheme $w = (a + bF_o + cF_o^2)^{-1}$ was used throughout the refinement, with $a = 4{\cdot}0$, $b = 1{\cdot}0$, and $c = 0{\cdot}005$.

Table 1 gives the final atomic parameters for the crystal-chemical unit: because of restrictions on the intensity data the values for b_{ij} are of almost no significance. Observed and calculated structure factors, based on the final atomic parameters, are listed in Supplementary Publication No. SUP 20633 (6 pp., 1 microfiche).* Bond distances and angles, within the formula unit, are listed in Table 2. A projection

TABLE 2

Molecular geometry within the formula unit, with estimated standard deviations in parentheses

(*a*) Distances (Å)

Co–Cl(1)	2·262(5)	N(2)–C(7)	1·483(29)
Co–Cl(2)	2·247(4)	N(3)–C(1)	1·360(29)
Co–S(1)	2·310(5)	N(3)–C(5)	1·480(20)
Co–S(2)	2·336(7)	N(4)–C(2)	1·348(25)
S(1)–C(1)	1·741(17)	N(4)–C(9)	1·443(19)
S(2)–C(2)	1·778(22)	C(3)–C(4)	1·55(3)
N(1)–C(1)	1·340(17)	C(5)–C(6)	1·58(3)
N(1)–C(3)	1·494(24)	C(7)–C(8)	1·55(2)
N(2)–C(2)	1·334(16)	C(9)–C(10)	1·46(3)

(*b*) Angles (°)

Cl(1)–Co–Cl(2)	109·4(0·2)	S(2)–C(2)–N(2)	117·7(1·5)
Cl(1)–Co–S(1)	110·4(0·2)	S(2)–C(2)–N(4)	120·8(1·1)
Cl(1)–Co–S(2)	110·7(0·2)	N(2)–C(2)–N(4)	121·5(1·8)
Cl(2)–Co–S(1)	116·1(0·2)	C(1)–N(1)–C(3)	121·6(1·8)
Cl(2)–Co–S(2)	111·2(0·3)	C(2)–N(2)–C(7)	119·9(1·6)
S(1)–Co–S(2)	98·6(0·2)	C(1)–N(3)–C(5)	120·3(1·7)
Co–S(1)–C(1)	106·0(0·5)	C(2)–N(4)–C(9)	122·1(1·8)
Co–S(2)–C(2)	109·5(0·5)	N(1)–C(3)–C(4)	107·8(2·1)
S(1)–C(1)–N(1)	117·6(1·6)	N(3)–C(5)–C(6)	105·9(1·4)
S(1)–C(1)–N(3)	124·6(1·0)	N(2)–C(7)–C(8)	108·1(1·8)
N(1)–C(1)–N(3)	117·8(1·5)	N(4)–C(9)–C(10)	110·2(1·7)

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* For details see Notice to Authors No. 7 in *J. Chem. Soc.* (*A*), 1970, Index Issue No. 20.

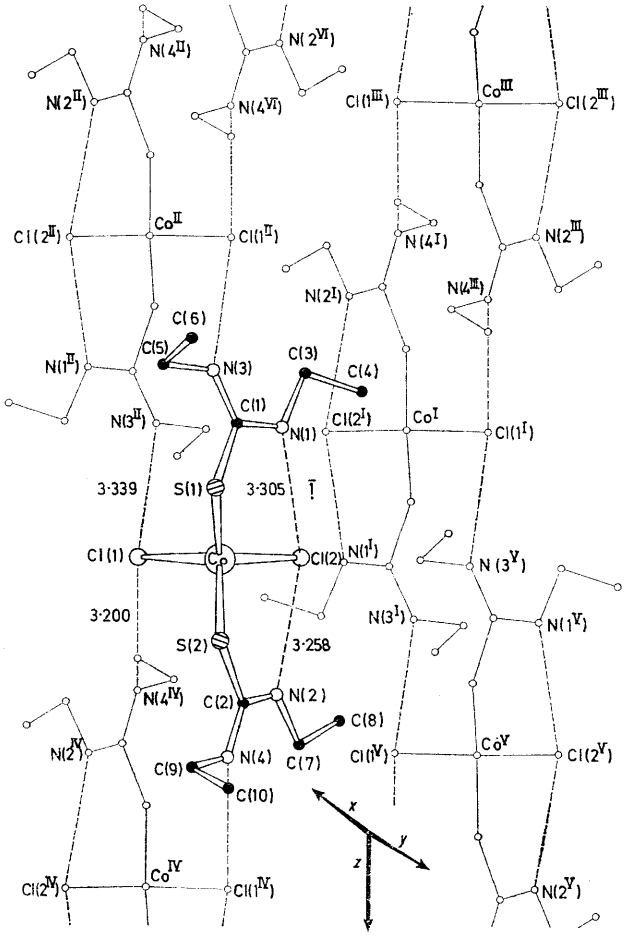
[2] O. Piovesana and C. Furlani, *J. Inorg. Nuclear Chem.*, 1969, **30**, 1249.

[3] G. Mazzone, A. Vaciago, and M. Bonamico, *Ricerca sci.*, 1963, **33**, (II*A*), 1113.

[4] D. C. Phillips, *Acta Cryst.*, 1954, **7**, 746.

of the structure with the hydrogen bond system is shown in the Figure.

Calculations.—Calculations were carried out on a Univac 1108 Computer of Rome University. Intensity corrections, scaling, Wilson plot, Fourier syntheses, and interatomic distances and angles were calculated by use of programmes written by Domenicano and Vaciago,[5] and for the structure-factor calculations and the least-squares refinement, the programmes written by Albano *et al.*[6] were used. Neutral atomic scattering factors, corrected for anomalous dispersion in the case of cobalt, chlorine, and sulphur,[7] were taken from ref. 8.



Projection of the structure on the (110) plane, showing the hydrogen bond system. Roman superscript numerals refer to the following equivalent positions:

I $-x, -y, -z$
II $1-x, -y, -z$
III $-1+x, y, -1+z$
IV $1-x, -y, 1-z$
V $-1+x, y, z$
VI $x, y, -1+z$

DISCUSSION

Description of the Structure.—The crystal structure consists of polymeric rows (parallel to the *c* axis) of molecules, related to each other by the centre of symmetry, and connected by hydrogen bonds between the chlorine and NH groups (see Figure). The criteria adopted for the existence of hydrogen bonds were N · · · Cl distances of <3·4 Å and angles of *ca.* ⩾150° subtended at hydrogen (analogous criteria were indicated by Luth and Truter [9]). There are several intermolecular distances between the carbon or nitrogen and sulphur atoms <4 Å. Molecules are more or less planar [except Cl(1) and the terminal carbon atom], the molecular form depending on the intramolecular hydrogen bonds: in fact, N(1)H and N(2)H groups are joined to the same chlorine atom [Cl(2)] with distances of 3·305 and 3·258 Å respectively.

A similar kind of structure is given by the type (*A*) molecules in dichlorobis(diethylthiourea)zinc(II): the analogy is underlined by a proper projection in the Figure.

The cobalt co-ordination is tetrahedral with a small but significant deviation of the bond angles around the cobalt atom from those of a regular tetrahedron. Values are: S–Co–S 98·6 (2), S–Co–Cl (mean) 112·1, and Cl–Co–Cl 109·4° (2); distortions are weaker than those observed [10] for the refined structure of dichlorobisthioureacobalt(II) [$Co(tu)_2Cl_2$], while preliminary results reported previously [11,12] do not permit an absolute comparison. The mean Co–S and Co–Cl bond lengths are 2·323 and 2·254 Å, similar to those found for $Co(tu)_2Cl_2$. The Co–S bond length (2·33 Å) is as in CoS.[13]

For the S–C bonds (mean 1·76 Å) and for sulphur-bonded carbon–nitrogen bonds (mean 1·345 Å) our values compare well with those found in thiourea, and several of its derivatives and co-ordination complexes.[1,14-17] For these particular SC–N bond lengths we did not note any shortening, which is present in $Co(tu)_2Cl_2$ [10] and which was emphasised by Kunchur and Truter [15] in $Zn(tu)_2Cl$ structure.

Bond angles for sulphur found in the complexes are approximately tetrahedral (mean 107·7°), and those around the sulphur-bonded carbon atom do not differ significantly from 120°. All other bond distances and angles in the ligand molecule are as expected.

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