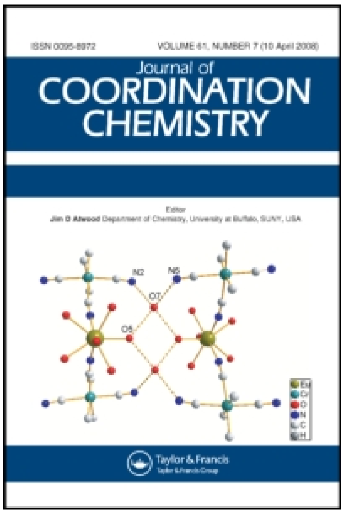

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X-RAY CRYSTAL STRUCTURE AND INFRARED SPECTRUM OF THE MONOCLINIC FORM OF DICHLOROBIS-(*N,N′*-DIETHYLTHIOUREA)COBALT(II)

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The monoclinic form of dichlorobis(*N,N′*-diethylthiourea)cobalt(II) [$CoCl_2$(*detu*)$_2$] (**1**) was synthesized and characterized by single crystal X-ray diffraction (space group $P2_1/c$, $a = 10.439(2)$, $b = 14.964(2)$, $c = 24.005(3)$ Å, $\beta = 92.00(1)°$, $Z = 8$). The solid state structure is described and compared with that of the triclinic form previously reported. The asymmetric unit consists of two independent complex molecules, in which the cobalt ions show distorted tetrahedral coordination by two sulfurs from the *detu* ligands and two chloride ions.

Keywords: Cobalt(II); cobalt halides; thiourea; hydrogen bonds; X-ray structure

INTRODUCTION

The dymorphism of dichlorobis(*N,N′*-diethylthiourea)cobalt(II) [$CoCl_2$-(*detu*)$_2$, where *detu* = *N,N′*-diethylthiourea] (**1**) was reported by Bonamico *et al.*,[1] who isolated both a triclinic and a monoclinic form for the title compound. The triclinic form consists of polymeric chains of complex molecules connected *via* intermolecular hydrogen bonds between chloride ions and HN groups from *detu* ligands. The structure of the monoclinic form was

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only suggested[2] on the basis of its isomorphism with $[ZnCl_2(detu)_2]$ (**2**) [$a = 10.453(5)$, $b = 14.981(1)$, $c = 24.044(5)$ Å, $\beta = 92.1(1)°$, space group $P2_1/c$]. In the present communication we report the solid-state structure of the monoclinic form of **1**, obtained by single crystal X-ray diffraction methods.

EXPERIMENTAL

Reagents

Metal salts and solvents were Aldrich products used without further purification.

Measurements

Elemental analyses were performed on an EA-1108 Fisons CHN-S instrument. The Co percentage was measured by means of a Varian Liberty 200 ICP emission spectrometer, using a water solution obtained after treatment of **1** with nitric acid. Infrared spectra were recorded on a Bruker IFS55 spectrometer at room temperature. Far-IR ($500-50\,cm^{-1}$) spectra (resolution $2\,cm^{-1}$) were recorded using polythene pellets with a Mylar beam-splitter and polythene windows. IR ($4000-500\,cm^{-1}$) spectra (resolution $4\,cm^{-1}$) were recorded using KBr pellets and chloroform solutions, with a KBr beam-splitter and KBr windows.

Synthesis of Dichlorobis(*N*,*N*′-diethylthiourea)cobalt(II) (1)

A variation of the literature[3] synthesis was used. $CoCl_2 \cdot 6H_2O$ (1.06 g, 4.45 mmol) and *N*,*N*′-diethylthiourea (1.12 g, 8.47 mmol) were suspended in $100\,cm^3$ of refluxing benzene with magnetic stirring. After two hours the solvent was removed to give a blue powder. The product was purified by recrystallization from hot methylene chloride and the degree of purification monitored by TLC. Obtained product: 1.70 g, yield 97%, m.p. 115°C. Elemental analysis (calculated in brackets) for $C_{10}H_{24}Cl_2CoN_4S_2$ (%): C 30.45 (30.46); H 6.40 (6.14); N 14.08 (14.21); S 16.66 (16.26); Co 14.08 (14.6). Crystals suitable for crystallographic analysis were obtained by slow evaporation of a benzene/CH_2Cl_2 solution of the title compound. Solid state FT-IR bands: 3274s, 3034w, 2979m, 2932w, 2873w, 1583vs, 1525vs, 1461w, 1449w, 1383m, 1344w, 1312m, 1260vs, 1161m, 1136m, 1094w, 1053s, 930s, 802s, 738m, 679w, 600s, 549m, 491m, 447m, 420m, 304vs, 143vs cm^{-1}.

X-Ray Structure Determination

Intensity data were collected at room temperature using a Siemens P4/RA automatic diffractometer equipped with graphite monocromator. No appreciable intensity decay was observed and only correction for Lorentz polarisation and absorption (ψ scans[4]) was applied. The structure was solved by direct methods with the program SIR 92,[5] which gave the positions of all non-hydrogen atoms, and refined using the SHELXL93[6] program package. Complex neutral atom scattering factors[7] were employed throughout. Details on crystal data, intensity collection and structure refinement are given in Table I. The C(16), N(7) and N(8) atoms were found to be disordered and modelled over two positions with occupancy factors refined to 0.723 and 0.277, respectively. All non-hydrogen atoms, with the exception of those involved in disorder, were refined with anisotropic thermal parameters. Hydrogen atoms were treated as fixed contributors in calculated positions and refined isotropically with $B(11) = 1.2B_{eq}(C)$. Selected

TABLE I Crystal data and structure refinement details for **1**

Empirical formula	$C_{10}H_{24}CoN_4S_2Cl_2$
Formula weight	394.28
Temperature	293(2) K
Radiation (λ, Å)	MoKα (0.71069)
Crystal system	monoclinic
Space group	$P2_1/c$
a (Å)	10.439(2)
b (Å)	14.964(2)
c (Å)	24.005(3)
β(0)	92.00(1)
Volume (Å^3)	3747.5(9)
ρ calc (g cm^{-3})	1.398
Z	8
F(000)	1640
μ(mm^{-1})	1.417
Crystal size (mm)	0.3 × 0.3 × 0.4
θ range (′)	2.18–30.00
Index ranges	$-l \leq h \leq 14$ $-l \leq k \leq 21$ $-33 \leq l \leq 33$
Reflections collected	13423
Independent reflections ($R_{int} = 0.0509$)	10906
Refinement method	Full-matrix least-squares on F^2
Data/restraints/parameters	10904/0 1 342
Goodness-of-fit on F^2	1.021
Final R indices [$I > 2\sigma(I)$	$R_1{}^{a} = 0.0599$, $wR_2{}^{b} = 0.1355$
R indices (all data)	$R_1{}^{a} = 0.1201$, $wR_2{}^{b} = 0.1704$
Largest diff. peak and hole (e Å^{-3})	0.644 and -0.632

[a] $R_1 = \sum(|F_o| - |F_c|)/|F_o|$.
[b] $wR_2 = [\sum w(F_o^2 - F_c^2)^2 / \sum wF_o^4]^{1/2}$ with $w = 1/[\sigma^2(F_o^2) + (0.0622P)^2 + 2.3697P]$, where $P = (F_o^2 + 2F_c^2)/3$.

TABLE II Selected bond lengths and angles for **1**

Bond lengths (Å)			
Co(1)–S(1)	2.3269(11)	Co(1)–S(2)	2.3225(11)
Co(1)–Cl(1)	2.2668(12)	Co(1)–Cl(2)	2.2590(13)
Co(2)–S(3)	2.3260(12)	Co(2)–S(4)	2.3170(12)
Co(2)–Cl(3)	2.263(2)	Co(2)–Cl(4)	2.2612(13)
S(1)–C(1)	1.729(4)	S(2)–C(6)	1.722(4)
S(3)–C(11)	1.725(4)	S(4)–C(16′)	1.721(14)
Bond angles (°)			
Cl(2)–Co(1)–Cl(1)	107.34(5)	Cl(2)–Co(1)–S(2)	110.29(5)
Cl(1)–Co(1)–S(2)	113.96(5)	Cl(2)–Co(1)–S(1)	114.02(5)
Cl(1)–Co(1)–S(1)	112.66(5)	S(2)–Co(1)–S(1)	98.57(4)
Cl(4)–Co(2)–Cl(3)	107.64(6)	Cl(4)–Co(2)–S(4)	114.39(5)
Cl(3)–Co(2)–S(4)	113.70(5)	Cl(4)–Co(2)–S(3)	112.84(5)
Cl(3)–Co(2)–S(3)	110.85(5)	S(4)–Co(2)–S(3)	97.27(5)
C(1)–S(1)–Co(1)	106.75(12)	C(6)–S(2)–Co(1)	106.04(12)
C(11)–S(3)–Co(2)	110.30(12)	C(16)–S(4)–Co(2)	107.9(5)
C(16)–S(4)–Co(2)	108.3(2)		

TABLE III Hydrogen bonding interactions for **1**

Atoms	*Distance* (Å)		*Angle* (°)
1···2···3	1···3	2···3	1···2···3
N(1)···H(N1)···Cl(1)	3.255	2.401	172
N(3)···H(N3)···Cl(1)	3.308	2.464	167
N(4)···H(N4)···Cl(2)[a]	3.289	2.501	153
N(5)···H(N5)···Cl(4)	3.260	2.407	171
N(6)···H(N6)···Cl(3)[b]	3.250	2.477	150
N(7)···H(N7)···Cl(3)	3.218	2.366	171

[a] $2 - x, -0.5 + y, 1.5 - z$; [b] $1 - x, -y, 1 - z$.

interatomic distances and angles are collected in Table II, while hydrogen bonds are reported in Table III. Atomic positions are given in Table IV. Major calculations were carried out on a Alpha 3000/800S computer.

RESULTS AND DISCUSSION

The asymmetric unit of the monoclinic form of **1** comprises two crystallographically independent molecules (namely A and B in Figure 1) characterized by a different arrangement of *detu* molecules. The Co(II) coordination sphere is occupied by two chloride ions and two *detu* molecules, the latter acting as monodentate ligands *via* the sulphur atoms, in a distorted tetrahedral fashion [Cl(2)–Co(1)–Cl(1), 107.34°; Cl(4)–Co(2)–Cl(3), 107.64°, S(2)–Co(1)–S(1), 98.57°; S(4)–Co(2)–S(3), 97.27°] with Co–S and Co–Cl bond lengths (See Table II) analogous to those of the triclinic form.[1] Inter- and intramolecular hydrogen bonding interactions (Table III) are found to

TABLE IV Atomic coordinates ($\times 10^4$) and equivalent isotropic displacement parameters ($Å^2 \times 10^3$) for $CoCl_2(SC(NHC_2H_5)_2)_2$. $U(eq)$ is defined as one third of the trace of the orthogonalized U_{ij} tensor

	x/a	y/b	z/c	U(eq)
Co(1)	9339(1)	−167(1)	7885(1)	51(1)
Co(2)	4501(1)	−2513(1)	5165(1)	58(1)
S(1)	7848(1)	984(1)	7930(1)	61(1)
S(2)	7932(1)	−1369(1)	7885(1)	61(1)
S(3)	3163(1)	−1298(1)	5307(1)	62(1)
S(4)	2965(1)	−3620(1)	5244(1)	72(1)
Cl(1)	10776(1)	−158(1)	8615(1)	76(1)
Cl(2)	10464(1)	−167(1)	7098(1)	67(1)
Cl(3)	5358(1)	−2446(1)	4313(1)	80(1)
Cl(4)	6138(1)	−2599(1)	5805(1)	83(1)
N(1)	9778(3)	1885(2)	8408(1)	57(1)
N(2)	8274(3)	2734(2)	7947(2)	65(1)
N(3)	9927(3)	−2244(2)	8328(1)	54(1)
N(4)	8509(3)	−3088(2)	7812(1)	57(1)
N(5)	5132(3)	−533(2)	5852(1)	52(1)
N(6)	3605(3)	413(2)	5494(1)	57(1)
C(1)	8693(3)	1941(2)	8110(2)	49(1)
C(2)	10564(4)	2647(3)	8598(2)	63(1)
C(3)	10044(5)	3100(3)	9098(2)	80(1)
C(4)	7108(5)	2935(3)	7623(2)	80(1)
C(5)	6120(5)	3288(6)	7957(3)	136(3)
C(6)	8860(3)	−2302(2)	8015(2)	47(1)
C(7)	10792(4)	−2971(3)	8471(2)	59(1)
C(8)	11785(6)	−2666(4)	8891(3)	102(2)
C(9)	7349(4)	−3277(3)	7468(2)	68(1)
C(10)	6281(5)	−3571(4)	7815(3)	102(2)
C(11)	4037(3)	−404(2)	5569(2)	45(1)
C(12)	5895(4)	167(3)	6122(2)	60(1)
C(13)	6985(5)	−224(4)	6457(2)	98(2)
C(14)	2419(4)	677(3)	5193(2)	67(1)
C(15)	1389(5)	869(5)	5584(3)	113(2)
C(16)	3341(5)	−4515(3)	4776(2)	49(1)
N(7)	4035(4)	−4394(3)	4330(2)	57(1)
N(8)	2889(5)	−5319(3)	4881(2)	66(1)
C(17)	4315(5)	−4988(4)	3940(2)	92(2)
C(18)	4790(7)	−4590(4)	3427(2)	112(2)
C(19)	1978(7)	−5515(4)	5306(3)	124(3)
C(20)	1271(7)	−6296(5)	5199(3)	133(3)
C(16′)	3698(13)	−4540(9)	5544(6)	53(3)
N(8′)	3123(12)	−5329(9)	5452(5)	61(3)
N(7′)	5114(12)	−5500(8)	4226(5)	59(3)

be very important in determining the overall crystal structure, and differentiate the monoclinic from the triclinic form. In the monoclinic form, two kinds of crystallographically independent units with different intramolecular hydrogen bonds, namely A and B, are present. Four intramolecular hydrogen bonding interactions are found among HN(1), Cl(1) and HN(3) in A, and between Cl(4) and HN(5), and Cl(3) and HN(7) in B (Figure 1).

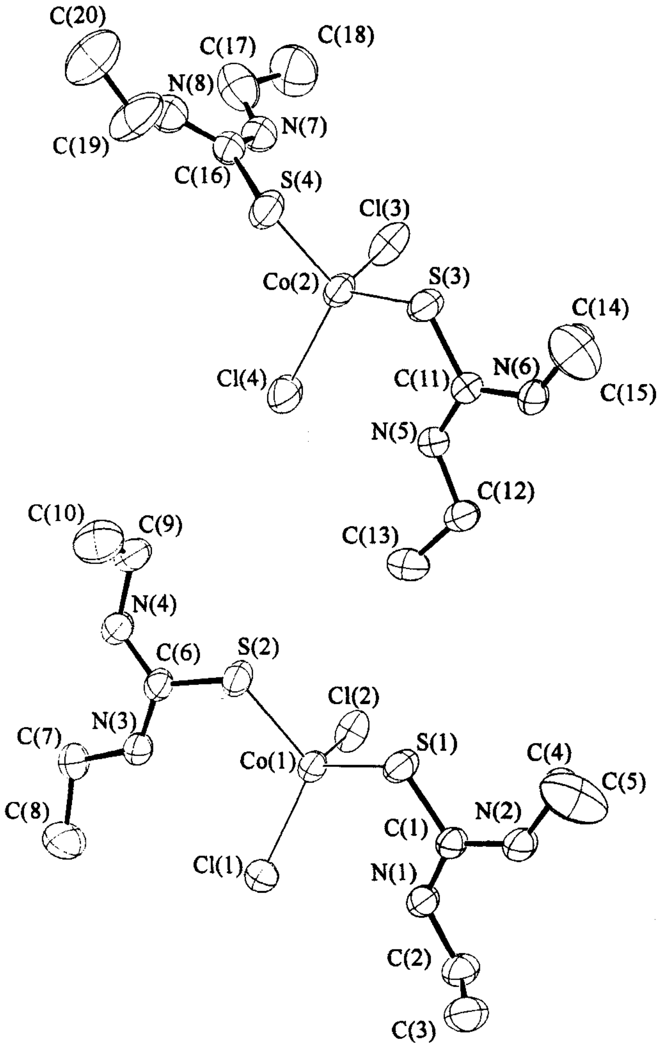

FIGURE 1 ORTEP view and labelling scheme of **1** (monoclinic form) units A and B (lower and upper drawing, respectively). Thermal ellipsoids for atoms are drawn at the 50% probability level. Hydrogen atoms have been omitted for clarity.

These interactions determine different conformations in the *detu* ligands. As far as the intermolecular interactions are concerned, the hydrogen HN(4) atom and the Cl(2) belonging to two different A units interact with each other, to produce a polymeric row parallel to the *b* axis. On the other hand, the interaction between HN(6) and Cl(3) of two B type units produces discrete dimers. The lattice is then built up by an alternance of parallel polymeric chains of A molecules and rows of dimeric units of B, where molecules are related by a centre of symmetry. The nature of this structure not only confirms the deductions by Bonamico *et al.*,[2] but also that the net of hydrogen bond interactions, described above, is responsible for the isomorphism between **1** and **2**. $Zn(tu)_2Cl_2$ and $Co(tu)_2Cl_2$ (tu = thiourea), in which this kind of bond is not present, are not isomorphous. As regards the infrared, the spectrum both in solution and in the solid state, is dominated by a set of bands from the thiourea ligands. The NH stretching modes are visible at $3274\,cm^{-1}$ in the solid state spectrum, whilst in chloroform solution two peaks are distinguishable: a broad band at $3257\,cm^{-1}$ and a sharp one at $3423\,cm^{-1}$, which might be assigned respectively to the stretching modes of NH involved in intramolecular hydrogen bonds, and to those of free NH. On the other hand, in the FIR region, the bands overlapping around $304\,cm^{-1}$ may be attributed to Co–Cl and Co–S stretching modes, according to the literature.[8]

Supplementary Material

Anisotropic and isotropic displacement parameters, hydrogen coordinates, and tables of observed and calculated structure factors are available from the authors on request.

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