Table 3. *Torsion angles* (°), *with standard deviations in parentheses, in the tetrahydrofuran molecules*

A positive rotation is anticlockwise when viewed from atom 3 to atom 2.

1 2 3 4	
O(1)–C(11)–C(12)–C(13)	160·3 (2·2)
C(11)–C(12)–C(13)–C(14)	−148·1 (2·3)
C(12)–C(13)–C(14)–O(1)	149·3 (1·1)
C(13)–C(14)–O(1)–C(11)	−150·7 (1·8)
C(14)–O(1)–C(11)–O(12)	−179·8 (1·8)
O(2)–C(15)–C(16)–C(17)	−168·7 (2·1)
C(15)–C(16)–C(17)–C(18)	174·9 (2·3)
C(16)–C(17)–C(18)–O(2)	176·6 (2·4)
C(17)–C(18)–O(2)–C(15)	−169·3 (4·0)
C(18)–O(2)–C(15)–C(16)	166·6 (2·5)

the Mo–O(2) bond makes a much larger angle, 16·90°, with the C(15), O(2), C(1) plane. The thermal motion in the tetrahydrofuran ligands is high and they are less than well defined. However, attempts to force the ligands to be planar or to have the more usual distortion by the use of constrained refinement pro-

duced models that were, according to statistical tests, worse than the unconstrained model.

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The Crystal Structure of Tetrakis[1-methylimidazoline-2(3H)-thione]cobalt(II) Diperchlorate

BY ERIC S. RAPER

Department of Chemistry, Newcastle upon Tyne Polytechnic, Newcastle upon Tyne NE1 8ST, England

AND IAN W. NOWELL

Department of Chemistry, Sheffield City Polytechnic, Sheffield S1 1WB, England

Abstract

[Co(C$_4$H$_6$N$_2$S)$_4$](ClO$_4$)$_2$, C$_{16}$H$_{24}$CoN$_8$S$_4^{2+}$. 2ClO$_4^-$, is tetragonal, $a = b = 12·359$ (4), $c = 19·932$ (4) Å, $Z = 4$, space group $I4_1/a$. $R = 0·0563$ for 1359 counter reflections. The ligand is monodentate and S-bonded to the metal [Co–S = 2·302 (1) Å]; the resultant CoS$_4$ tetrahedron is distorted by compression along the $\bar{4}$ axis. The discrete cations are grouped in pairs around symmetry centres. Distorted perchlorate anions with Cl–O = 1·306 (8), 1·375 (11) Å are H-bonded to the ligand by N–H$\cdots$O contacts of 2·872 Å.

Introduction

The preparation and characterization of complexes of 1-methylimidazoline-2(3H)-thione with Co^{II} and Zn^{II}

halides and perchlorates have been described (Raper & Brooks, 1977). In these complexes the potentially ambidentate ligand was shown to be monodentate with metal–S rather than metal–N contacts. This X-ray study has been undertaken in order to verify the conclusions drawn from infrared and visible spectra and to provide detailed information on the coordination geometry.

Experimental

Crystal data

Deep-green, well formed crystals of the complex were obtained from anhydrous ethanol containing 5% (v/v) triethyl orthoformate. Cell constants were obtained from Weissenberg and precession photographs;

Table 1. *Crystal data*

$C_{16}H_{24}CoN_8S_4^{2+} \cdot 2ClO_4^-$
FW 715·33
Tetragonal
$a = b = 12·359$ (4), $c = 19·932$ (4) Å
$V = 3044·76$ Å^3
$D_c = 1·56$ Mg m^{-3}
$D_m = 1·54$ (flotation)
$F(000) = 1452$

Reflection conditions:
$hkl: h + k + l = 2n$
$hk0: h, (k) = 2n$
$00l: l = 4n$
Space group: $I4_1/a$
$Z = 4$
μ(Mo $K\alpha$) = 0·992 mm^{-1}

systematic absences uniquely identified the space group $I4_1/a$. Crystal data are summarized in Table 1.

Data collection and reduction

A crystal 0·6 × 0·5 × 0·35 mm was mounted with a coincident with the rotation (ω) axis on an automated Stoe two-circle diffractometer. With monochromated Mo $K\alpha$ radiation ($\lambda = 0·71069$ Å) and the background–ω scan–background technique, 1728 unique reflections were measured of which 1359 had $I \geq 2·5\sigma(I)$ and were considered to be observed.

Structure determination and refinement

The Co atoms occupy sites of $\bar{4}$ symmetry with all their positional coordinates fixed. The Cl atoms occupy sites of twofold symmetry with x and y fixed. The asymmetric unit therefore contains, in addition to Co and Cl, one ligand molecule and two perchlorate O atoms.

The z coordinate of the Cl atom and the coordinates of the S atom were located by Patterson methods. The remaining non-H atoms were obtained by Fourier methods. These parameters were refined by full-matrix least-squares calculations with anisotropic temperature factors.

The coordinates of the H atoms attached to the heterocyclic atoms were located by difference methods but were not refined; their isotropic temperature factors were refined collectively [final $U = 0·120$ (15) Å^2]. Methyl H atoms were refined as a rigid group (C—H = 1·08 Å) and one overall isotropic temperature factor [final $U = 0·146$ (11) Å^2].

The function minimized was $\sum w(\Delta F)^2$ with $w = 0·8491/[\sigma^2(F) + 0·0088(F)^2]$. The final $R = 0·0563$ and $R_w = 0·0674$.

Scattering factors for non-H atoms were from Cromer & Liberman (1970) and from Stewart, Davidson & Simpson (1965) for H.

Positional parameters are in Table 2.*

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* Lists of structure factors and anisotropic thermal parameters have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 34324 (8 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Table 2. *Fractional positional parameters* ($\times 10^4$) *with e.s.d.'s in parentheses*

	x	y	z
Co	5000	7500	1250
Cl	5000	2500	2329 (2)
S	4758 (1)	5835 (1)	754 (1)
N(1)	6853 (3)	5641 (3)	300 (2)
N(3)	6421 (4)	4464 (3)	1032 (2)
C(1)	6792 (5)	6550 (5)	−179 (3)
C(2)	6042 (3)	5313 (3)	696 (2)
C(4)	7460 (5)	4244 (5)	857 (3)
C(5)	7747 (4)	4983 (5)	401 (3)
O(1)	4861 (12)	1555 (8)	2054 (7)
O(2)	4132 (12)	2727 (13)	2798 (8)
H(3)	6054	4205	1447
H(4)	7922	3652	1078
H(5)	8443	4899	183
H(11)	7517	6557	−480
H(12)	6700	7323	68
H(13)	6099	6401	−495

Description and discussion of the structure

Relevant distances and angles are in Table 3. Fig. 1 contains a labelled diagram of the cation with an adjacent perchlorate group; H atoms take the number of the atom to which they are attached, the methyl H atoms are 11, 12 and 13. The unique O atoms of the perchlorate group are 1 and 2. Fig. 2 shows the cell contents and H-bonding in the a projection.

The ligand is monodentate and S-bonded to the metal (Fig. 1). The CoS$_4$ tetrahedron is irregular, being compressed along the $\bar{4}$ axis. Two of the S—Co—S angles are 129·1 (1)°, the other four are 100·6 (0)°. This distortion generates long and short S$\cdots$S contacts (4·158 and 3·694 Å). The four Co—S bonds are identical [2·302 (1) Å] and are in the range normally observed for σ-bonded, tetrahedral Co^{II}—S systems (Spofford & Amma, 1976; Manojlović-Muir & Muir, 1974).

Among thiourea complexes of transition metals, M—S distances, M—S—C angles, and the angle between the M—S—C plane and the mean plane of the ligand are the parameters which have been used in assessing the character of the S atom and the nature of the metal–tu bond. In [Co(tu)$_4$](NO$_3$)$_2$.H$_2$O (Spofford & Amma, 1976), all the Co—S distances are in the range 2·291 to 2·302 Å. Three of the Co—tu contacts appear to be normal with Co—S—C angles in the range 108·2 to 110·6° and dihedral angles in the range 25·4 to 33·6°. In these instances the S atom is considered to be sp^2 hybridized. The remaining contact is atypical, however, with Co—S—C = 103·0° and the dihedral angle 75·8°. The authors suggest that the atypical molecule is bonded to Co through a $p\pi$ molecular orbital on the S atom. The geometry of the metal–ligand contacts in this report is very similar to that observed for the atypical tu molecule in the complex just described. We

suggest an alternative interpretation for the bonding in our complex, however. The Co—S—C angle (104·2°) indicates that the S atom is largely sp^3 in character.

Table 3. *Bonding and non-bonding distances* (Å) *and angles* (°) *with e.s.d.'s in parentheses*

Symmetry code

None *xyz*; (') $-x$, $\frac{1}{2} - y$, *z*; ('') $\frac{3}{4} + y$, $\frac{1}{4} - x$, $\frac{1}{4} - z$.

(*a*) The coordination sphere

Co—S	2·302 (1)	Co—S—C(2)	104·2 (1)
S···S''	3·694	S—Co—S'	129·1 (1)
S···S'	4·158	S—Co—S''	100·6 (0)

(*b*) The ligand molecule

C(2)—S	1·717 (4)	S—C(2)—N(1)	128·1 (4)
C(2)—N(1)	1·339 (5)	S—C(2)—N(3)	126·1 (3)
C(2)—N(3)	1·330 (6)	C(2)—N(3)—C(4)	111·2 (5)
N(3)—C(4)	1·358 (8)	N(3)—C(4)—C(5)	106·8 (5)
C(4)—C(5)	1·337 (9)	C(4)—C(5)—N(1)	106·8 (5)
C(5)—N(1)	1·387 (7)	C(5)—N(1)—C(2)	109·4 (4)
N(1)—C(1)	1·474 (7)	H(3)—N(3)—C(2)	120·7 (4)
N(3)—H(3)	0·996 (4)	H(3)—N(3)—C(4)	125·4 (4)
C(4)—H(4)	1·027 (6)	H(4)—C(4)—N(3)	123·9 (7)
C(5)—H(5)	0·969 (5)	H(4)—C(4)—C(5)	129·1 (6)
		H(5)—C(5)—C(4)	117·8 (6)
		H(5)—C(5)—N(1)	134·8 (7)
		C(1)—N(1)—C(5)	125·5 (5)
		C(1)—N(1)—C(2)	125·0 (5)
		N(1)—C(2)—N(3)	105·8 (4)

(*c*) The perchlorate group

Cl—O(1)	1·302 (8)	O(1)—Cl—O(1')	130·2 (1·4)
Cl—O(2)	1·450 (11)	O(2)—Cl—C(2')	99·7 (1·4)
O(1)···O(2')	2·130	O(1)—Cl—O(2)	110·4 (1·1)
O(1)···O(1')	2·361	O(1)—Cl—O(2')	101·3 (1·1)
O(2)···O(2')	2·217		
O(2)···O(1)	2·261		

Corrected for thermal motion

Cl—O(1)	1·306
Cl—O(2)	1·375

(*d*) Hydrogen bonds

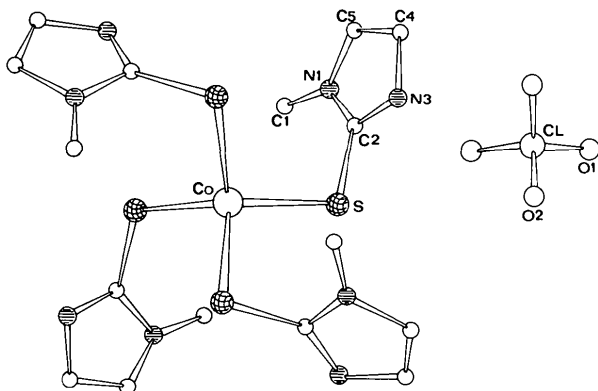|	
H(3)···O(1')	1·904
N(3)···O(1')	2·872

Fig. 1. Labelled diagram of the cation and neighbouring perchlorate group.

Furthermore, the unusual dihedral angle (68·3°) arises because the ligand is twisted out of the Co—S—C plane in order to facilitate H-bonding between the N(3)—H(3) group and O(1) of a neighbouring perchlorate anion (Fig. 1). Other instances where *M*—S—C angles appear to indicate tetrahedral S include ethylenethiourea in [Cu^I(etu)₄](NO₃) (Battaglia, Corradi, Nardelli & Vidoni Tani, 1976) and imidazoline-2-thione in [Cd*L*₂Cl₂] (Cavalca, Domiano, Musatti & Sgarabotto, 1968).

The ligand is essentially planar (Table 4), the largest displacement being that of N(1). The Co atom is significantly displaced (2·062 Å) from the mean plane of the ligand.

Comparison of bond lengths in the ligand with those in related molecules (Ansell, 1972; Form, Raper & Downie, 1976; Wheatley, 1953) as well as their metal complexes (Kheddar, Protas, Le Baccon, Guglielmetti & Guerchais, 1976; Battaglia *et al.*, 1976; Holt, Holt & Watson, 1970) shows the C—N distances [1·339 (5) and 1·330 (6) Å] in the thioamido moiety to be characteristically shorter than those involving the ethylenic C atoms [1·358 (8) and 1·387 (7) Å]. The rather long C(2)—S distance [1·717 (4) Å] suggests this bond to be largely *σ* in character and supports the previous assertion that the S atom is primarily sp^3.

Large temperature factors, significant variations in Cl—O bonds as well as O···O non-bonded contacts and large deviations from the tetrahedral value for the O—Cl—O angles all indicate that the perchlorate group is distorted (Camerman, Jensen & Balaban, 1969). Librational corrections (Schomaker & Trueblood, 1968) improved the agreement between the Cl—O distances and showed O(2), and its symmetry-related partner, to be the atoms most affected by thermal motion. The relative thermal inactivity of O(1) undoubtedly results from its involvement in H-bonding.
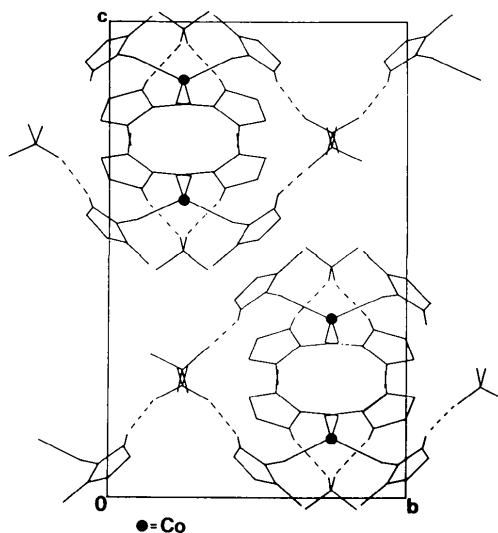

Fig. 2. Unit-cell contents and H-bonding in the *a* projection.

Table 4. *Equations of mean planes with atomic displacements*

The equation of the plane is $lX + mY + nZ - P = 0$ where X, Y and Z are fractional coordinates and P is the origin-to-plane distance in Å.

Plane	Atoms (displacements in Å)		Equation
1	Co S	C(2)	$-0.1047X - 0.4184Y + 0.9022Z + 2.2770 = 0$
2	S(−0.002)	C(2)(0.007)	$0.3102X + 0.6096Y + 0.7294Z - 7.3196 = 0$
	N(1)(−0.002)	N(3)(−0.002)	
3	S(−0.008)	C(2)(0.012)	$0.3173X + 0.6113Y + 0.7250Z - 7.3725 = 0$
	N(1)(0.014)	C(4)(−0.011)	
	C(5)(0.001)	N(3)(0.001)	
	C(1)(−0.009)		

Displacement of Co atom
from plane 3 = 2.062

Dihedral angles (°) with e.s.d.'s in parentheses

P1 and P2	68.3 (1.5)
P1 and P3	68.6 (1.5)
P2 and P3	0.5 (1.0)

Within the unit cell the four cations are grouped in pairs around symmetry centres (Fig. 2). Two types of H-bond involving N(3)−H(3)···O(1) contacts (2.872 Å) occur. One type involves both O(1) atoms from the same perchlorate group and N−H groups from different ligands but in the same cation; in the other case, O(1) atoms link N−H groups from neighbouring cations into extended chains of H-bonds along **b**.

All calculations were performed on the NUMAC IBM 370/167 computer at the University of Newcastle upon Tyne, England. *SHELX* (Sheldrick, 1976) and related programs were used in the analysis.

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The Crystal Structure of Δ,Λ-μ-Hydroxo-bis[bis(ethylenediamine)hydroxochromium(III)] Triperchlorate Monohydrate

BY KAREN KAAS

Chemistry Department, Royal Veterinary and Agricultural University, DK 1871 Copenhagen V, Denmark

Abstract

[(OH)(en)$_2$Cr(OH)Cr(en)$_2$(OH)](ClO$_4$)$_3$.H$_2$O, [Cr$_2$(C$_2$H$_8$N$_2$)$_4$(OH)$_3$](ClO$_4$)$_3$.H$_2$O, C$_8$H$_{35}$Cr$_2$N$_8$O$_3^{3+}$. 3ClO$_4^-$.H$_2$O, crystallizes in space group $P2_1/c$, with $a = 12.426$ (6), $b = 12.027$ (4), $c = 18.343$ (7) Å, $\beta = 104.13$ (4)°, $Z = 4$. The structure was refined to $R = 0.072$ for 3604 diffractometer intensities. The conformation of the complex ion is $^\delta_\lambda ΔΛ^\delta_\lambda$ and the Cr···Cr separation is 3.677 (2) Å. The complex ion has an intra-