[Li—O 1·943–1·961 (2) Å] (Klapper & Küppers, 1973) both of which show Li tetrahedrally coordinated to four O atoms. Five-coordinate Li has been observed in lithium antamanide (Karle, 1974) with four carbonyl O atoms and a CH_3CN N atom ligating Li^+ (Li—O 2·21 Å). The cryptate (211) offers six coordination sites to the encapsulated Li^+ ion with four O and two N sites [Li—O 2·081 (6)–2·173 (24) Å] in distorted octahedral array (Moras & Weiss, 1973). Thus Li—O distances increase with increasing coordination number.

The five-coordinate structures Li(1,5,9,13-tetra-oxacyclohexadecane)SCN (Groth, 1981a) (III) and Li(1,4,7,10-tetraoxacyclododecane)SCN (Groth, 1981b) (IV), where the four Li—O_{crown} distances average 2·07–2·09 Å in (III) and 2·057 (10) Å in (IV) (the fifth ligand in each is N), provide better comparison to the title structure.

Bond angles and distances within the crown-ether ring appear normal. The single ethylene (O—CH_2—CH_2—O) group is dimethyl substituted and thus shorter [C—C 1·47 (2) Å]. C—O distances of the type O—CH_2 [1·41 (2) Å] are comparable to the 1·43 (1) Å observed in (III) and (IV). C—C distances in O—C—C—C—O linkages [1·51 (2) Å] are similar to the 1·51 (1) Å observed in (IV).

The chirality of (II) as indicated by better refinement in the R,R modification is exactly as expected considering the starting material and synthetic technique (Malpass, Palmer & Ghirardelli, 1980). Other spectroscopic evidence has also been given which supports the conclusion that strong ion-pair bonding between the crown-complexed Li^+ ion and NO_3^- persists in solution as long as the polarity and donicity of the solvent are low. For example, the NO_3^- n–π^* CD is annulled in solutions of Li(6,7-dimethylbenzo-14-crown-4)NO_3 in CF_3CH_2OH, a polar, anion-solvating solvent; whereas the CD in CH_3CN is almost as great as it is in $CHCl_3$, a reflection of the rather modest donicity of acetonitrile (Gurman, 1968).

Similar solution CD evidence of strong metal–nitrate ion pairing in $CHCl_3$, CH_2Cl_2, CH_3CN and other low-donicity solvents and solvent mixtures for $LiNO_3$, $NaNO_3$, $Zn(NO_3)_2$ and other metal nitrates complexed with 6,7-dimethylbenzo-14-crown-4 and its hydrogenated analog, as well as with chiral 12-crown-4, 15-crown-5 and 18-crown-6 rings has been observed. A more extensive description of this work is in preparation (Malpass & Palmer, 1984) and further structural studies are in progress (Holt, 1984).

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Structure and Absolute Configuration of (−)₅₈₉-[2-(Methylthio)propionato-*S,O*][tris(2-aminoethyl)amine]cobalt(III) Diperchlorate, [Co(C₄H₇O₂S)(C₆H₁₈N₄)](ClO₄)₂

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Abstract. $M_r = 523·2$, orthorhombic, $P2_12_12_1$, $a = 11·346$ (1), $b = 15·554$ (2), $c = 11·044$ (1) Å, $V = 1949·0$ (4) Å³, $Z = 4$, D_m(ethanol/tetrabromoethane) = 1·78 (2), $D_x = 1·78$ Mg m⁻³, Mo $K\alpha_1$, $\lambda = 0·70926$ Å, $\mu = 1·31$ mm⁻¹, $F(000) = 1080$, $T = 297$ (2) K, final R is 0·042 for 2310 observed unique reflections. The Co atom is surrounded octahedrally by four N atoms of N(CH₂CH₂NH₂)₃ (tren) and S and O

atoms of $CH_3SCH(CH_3)COO^-$, where the S atom is *trans* with respect to the tertiary N atom of tren. The absolute configuration around the ligating S and the asymmetric C atom has been determined to be S and R, respectively.

Introduction. Generally, the rate of racemization of a Co^{III} complex at the coordinated thioether sulfur is so fast that it is impossible to isolate the complex with a chiral S atom. The inversion at the S atom is, however, hindered for the title complex by the steric interaction between two methyl groups attached to S and the adjacent C atoms. The chirality of the S atom is reflected in the circular dichroism (CD) spectra in the Co^{III}–S charge-transfer (CT) region (Kojima & Fujita, 1983). The crystal structure analysis has been undertaken to establish the relation between the CD spectra and the absolute configuration of the coordinated thioether S atom.

Experimental. Separation by column chromatography showed that only one of the geometrical isomers of the $[Co\{SCH(CH_3)COO\}(tren)]^+$ complex was yielded by the reaction of cis-$[CoCl_2(tren)]^+$ with racemic $HSCH(CH_3)COOH$. The title compound $[Co\{CH_3SCH(CH_3)COO\}(tren)]^{2+}$ was prepared by methylation of the optically active thiolato complex (Kojima & Fujita, 1983). Crystals obtained from an

aqueous solution of pH ca 2 at 277 K were kindly supplied by Professor J. Fujita, Nagoya University, in the form of orange-red prisms, grown along **a**. Crystal $0.3 \times 0.5 \times 0.55$ mm, Rigaku AFC-5 four-circle diffractometer, graphite monochromator, Laue group mmm, cell parameters refined by least-squares methods on the basis of 20 2θ values, $30 < 2\theta < 37°$, intensity measurement performed to $2\theta = 55°$ $(+h, +k, +l$ set), θ–2θ scan, scan speed $2°$ min^{-1} (θ); mean ratio of structure factors of the five standard reflections was $0.98 < \sum(|F_o|/|F_o|_{\text{initial}})/5 \leq 1.00$; space group $P2_12_12_1$ determined from systematic absences $h00$, h odd, $0k0$, k odd, $00l$, l odd; 2585 reflections measured, 2310 observed unique reflections with $|F_o| > 3\sigma(|F_o|)$; corrections for Lorentz–polarization and for absorption $[1.20 < (A^*)^{1/2} < 1.37]$; structure solved by Patterson–Fourier methods, refined by block-diagonal least squares with anisotropic thermal parameters for all non-H atoms; 22 among 25 H atoms found on difference density maps and others calculated, H atoms included in refinement with isotropic thermal parameters; $\sum w||F_o| - |F_c||^2$ minimized, $w^{-1} = \sigma^2(|F_o|) + (0.015|F_o|)^2$; final $R = 0.042$, $wR = 0.054$, $S = 2.5$ for 2310 unique reflections;† reflection/parameter ratio was 7.1; all shifts in final cycle of refinement $< \sigma$ for non-H atoms and 2σ for H atoms; the max. and min. $\Delta\rho$ excursions in final difference density maps 1.0 and -0.6 e Å^{-3}, respectively; complex neutral-atom scattering factors from *International Tables for X-ray Crystallography* (1974); computation program system *UNICS*III (Sakurai & Kobayashi, 1979); final atomic parameters are presented in Table 1.

The absolute structure was determined by an anomalous-scattering technique. The intensities of the $+h,-k,+l$ set were also measured to a 2θ value of $40°$ and 957 reflections were observed above the threshold. The observed and calculated intensity differences, $\Delta|F|$ $[= |F(hkl)| - |F(h\bar{k}l)|]$ for which $|F_o(hkl)|$ and $|F_o(h\bar{k}l)|$ differed by more than 15% and more than 3.0 in magnitude, are compared in Table 2. The concordance of the signs of $\Delta|F|_{\text{obs}}$ and $\Delta|F|_{\text{calc}}$ indicates that the absolute crystal structure listed in Table 1 is correct. In order to confirm the absolute configuration, a refinement was made separately with the enantiomeric structure. It converged to $R=0.050$ and $wR=0.064$ for 2310 unique reflections and could be rejected at the 0.005 significance level by the Hamilton (1965) test.

Table 1. *Positional parameters* ($\times 10^4$; *for* Co, S *and* Cl $\times 10^5$) *and equivalent isotropic temperature factors (Hamilton, 1959)*

	x	y	z	B_{eq}(Å^2)
Co	17094 (5)	22927 (4)	84818 (6)	1.8
S	6566 (10)	15580 (8)	98498 (12)	2.5
O(1)	2936 (3)	2284 (2)	9656 (3)	2.5
O(2)	3690 (3)	1820 (3)	11378 (4)	3.1
N(1)	2651 (4)	3009 (3)	7401 (4)	2.5
N(2)	2506 (4)	1309 (3)	7729 (4)	2.6
N(3)	475 (4)	2326 (3)	7260 (4)	2.7
N(4)	1181 (4)	3372 (3)	9211 (4)	2.5
C(1)	1556 (6)	969 (4)	12018 (6)	3.8
C(2)	1909 (5)	1185 (3)	10740 (5)	2.6
C(3)	2905 (4)	1818 (3)	10615 (4)	2.2
C(4)	103 (6)	550 (5)	9235 (6)	4.4
C(5)	3750 (5)	2512 (3)	7150 (6)	3.2
C(6)	3420 (6)	1612 (4)	6841 (6)	4.3
C(7)	1984 (5)	3190 (5)	6249 (5)	4.1
C(8)	669 (6)	3083 (5)	6456 (6)	4.4
C(9)	2934 (5)	3811 (3)	8090 (6)	3.4
C(10)	1797 (6)	4133 (3)	8663 (6)	3.7
Cl(1)	6832 (15)	4700 (9)	50524 (12)	3.5
O(11)	605 (4)	302 (3)	6330 (4)	4.7
O(12)	1858 (7)	686 (8)	4790 (7)	14.1
O(13)	−67 (10)	1042 (8)	4702 (8)	21.3
O(14)	632 (6)	−317 (4)	4447 (5)	8.0
Cl(2)	19749 (13)	36618 (10)	26938 (14)	3.6
O(21)	1279 (4)	3099 (3)	1955 (5)	5.2
O(22)	1278 (4)	4140 (3)	3531 (5)	5.1
O(23)	2526 (7)	4252 (4)	1862 (7)	10.4
O(24)	2855 (6)	3204 (5)	3299 (6)	9.5

† Lists of structure factors, anisotropic thermal parameters, atomic parameters for H atoms and bond lengths and bond angles involving H atoms and those in the perchlorate ions have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 39020 (26 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Table 2. *Determination of the absolute configuration*

h	k	l	$|F(hkl)| - |F(h\bar{k}l)|$ obs.	calc.
5	1	1	5·1	4·2
8	1	3	−3·1	−3·2
4	2	7	3·7	3·4
10	2	3	−4·3	−3·7
4	7	1	−3·5	−2·6
7	7	6	−3·9	−2·6
4	8	2	3·4	1·0

Discussion. There are two possible geometrical isomers for the title complex, the t and p isomers, where the S atom of 2-(methylthio)propionato is *trans* with respect to the tertiary or a primary N atom, respectively. The complex cation is a t isomer as shown in Fig. 1. The absolute configuration around the S and C(2) atoms are S and R, respectively. The present complex shows a positive CD peak at *ca* 34 000 cm⁻¹ (Kojima & Fujita, 1983). Thus, the absolute configuration of the ligating sulfide S atom is expected to be S when a positive CD peak is observed in the Co^III–S CT region.

The five-membered chelate ring formed by 2-(methylthio)propionato has an envelope conformation as shown in Fig. 2. The C(2) and C(3) atoms deviate from the plane defined by Co, S and O(1) by 0·616 (6) and 0·212 (7) Å, respectively. The torsion angle C(1)–C(2)–S–C(4) which involves two methyl groups is −89·6 (4)°. Bond lengths and angles are listed in Table 3. S–Co–N(2) of 97·7 (1)° is larger than S–Co–N(4) [89·8 (1)°], suggesting a steric interaction between the methyl group C(4) and the N(2) atom. Co–N bond lengths of tren show no significant difference from each other. The coordinated thioether S atom, which has a formal neutral charge, does not appear to exert a structural *trans* effect in accordance with the reported experimental results (Elder, Kennard, Payne & Deutsch, 1978). The Co–S bond distance of 2·239 (1) Å is significantly shorter than the values of 2·252–2·274 Å for other thioether complexes (Elder *et al.*, 1978; Isago, Okamoto, Ohmasa & Hidaka, 1980). It may be a structural *trans* effect of the tren ligand that the bond between Co and the atom *trans* with respect to the tertiary N atom is shortened. Such a *trans* effect of tren was also recognized in [Co(gly)(tren)]²⁺ (Mitsui, Watanabe, Harada, Sakamaki & Iitaka, 1976).

The thermal parameters for the perchlorate O atoms are high. It may be a result of structural disorder. Cl–O bond lengths and O–Cl–O angles are in the range from 1·29 (1) to 1·44 (1) Å and from 98·6 (6) to 115·7 (6)°, respectively.*
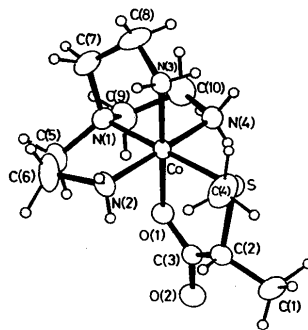
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* See deposition footnote.

Fig. 1. An *ORTEP* drawing of the complex cation with thermal ellipsoids scaled at the 50% probability level (Johnson, 1965). H atoms are represented by circles of radius 0·08 Å.
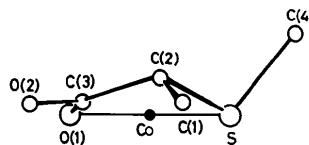

Fig. 2. The S–O ligand viewed along the line through the Co atom and the midpoint of the S–O(1) axis.

Table 3. *Bond lengths (Å) and angles (°)*

Co–S	2·239 (1)	N(1)–C(7)	1·507 (7)
Co–O(1)	1·902 (3)	N(1)–C(9)	1·496 (7)
Co–N(1)	1·951 (5)	N(2)–C(6)	1·503 (8)
Co–N(2)	1·962 (5)	N(3)–C(8)	1·491 (9)
Co–N(3)	1·946 (5)	N(4)–C(10)	1·502 (7)
Co–N(4)	1·956 (5)	C(1)–C(2)	1·505 (9)
S–C(2)	1·823 (6)	C(2)–C(3)	1·505 (7)
S–C(4)	1·820 (8)	C(5)–C(6)	1·489 (8)
O(1)–C(3)	1·284 (6)	C(7)–C(8)	1·519 (9)
O(2)–C(3)	1·226 (6)	C(9)–C(10)	1·522 (9)
N(1)–C(5)	1·493 (7)		
		Co–N(1)–C(7)	110·4 (3)
S–Co–O(1)	85·8 (1)	Co–N(1)–C(9)	106·4 (3)
S–Co–N(1)	174·9 (1)	C(5)–N(1)–C(7)	111·1 (4)
S–Co–N(2)	97·7 (1)	C(5)–N(1)–C(9)	110·3 (4)
S–Co–N(3)	95·6 (1)	C(7)–N(1)–C(9)	112·4 (4)
S–Co–N(4)	89·8 (1)	Co–N(2)–C(6)	110·5 (4)
O(1)–Co–N(1)	91·2 (2)	Co–N(3)–C(8)	109·1 (4)
O(1)–Co–N(2)	86·9 (2)	Co–N(4)–C(10)	111·6 (3)
O(1)–Co–N(3)	178·5 (2)	S–C(2)–C(1)	111·7 (4)
O(1)–Co–N(4)	87·1 (2)	S–C(2)–C(3)	109·1 (3)
N(1)–Co–N(2)	86·2 (2)	C(1)–C(2)–C(3)	115·6 (5)
N(1)–Co–N(3)	87·4 (2)	O(1)–C(3)–O(2)	123·1 (4)
N(1)–Co–N(4)	86·0 (2)	O(1)–C(3)–C(2)	117·7 (4)
N(2)–Co–N(3)	93·4 (2)	O(2)–C(3)–C(2)	118·9 (4)
N(2)–Co–N(4)	170·1 (2)	N(1)–C(5)–C(6)	108·6 (5)
N(3)–Co–N(4)	92·4 (2)	N(2)–C(6)–C(5)	108·6 (5)
Co–S–C(2)	96·3 (2)	N(1)–C(7)–C(8)	110·2 (5)
Co–S–C(4)	111·8 (2)	N(3)–C(8)–C(7)	108·7 (5)
C(2)–S–C(4)	101·3 (3)	N(1)–C(9)–C(10)	107·7 (5)
Co–O(1)–C(3)	123·1 (3)	N(4)–C(10)–C(9)	107·6 (4)
Co–N(1)–C(5)	106·0 (3)		

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The Structure of Dicarbonyl(η^5-cyclopentadienyl) (η^3-2-methylallyl)molybdenum(II), [Mo(C$_4$H$_7$)(C$_5$H$_5$)(CO)$_2$]

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Abstract. $M_r = 272 \cdot 2$, monoclinic, $P2_1/n$, $a = 6 \cdot 1105$ (9), $b = 12 \cdot 7885$ (22), $c = 13 \cdot 7247$ (24) Å, $\beta = 98 \cdot 787$ (13)°, $U = 1059 \cdot 91$ Å^3, $D_x = 1 \cdot 705$ Mg m^{-3}, $Z = 4$, $F(000) = 544$ e, $\bar{\lambda}$(Mo $K\alpha$) = $0 \cdot 71069$ Å, $\mu = 1 \cdot 083$ mm^{-1}, $T = 188$ K. $R = 0 \cdot 025$ for 2867 unique reflections. The molecule crystallizes with the η^3-2-methylallyl ligand in the endo conformation, and the three Mo—C(allyl) distances are equal within experimental error, average $2 \cdot 3163$ (13) Å.

Introduction. There is currently considerable theoretical and experimental interest in the structural preferences of complexes containing the η^3-allyl or a substituted η^3-allyl ligand. Detailed NMR studies (Faller, Chen, Mattina & Jakubowski, 1973) had previously established that whilst both exo and endo (Schilling, Hoffmann & Faller, 1979) conformations of [(η^5-C$_5$H$_5$)(2-R-η^3-C$_3$H$_4$)(CO)$_2$Mo] (R = H, Me) are present (and rapidly interconvert) in solution, the major isomer is exo for R = H and endo for R = Me. It is, furthermore, exo-[(η^5-C$_5$H$_5$)(η^3-C$_3$H$_5$)(CO)$_2$Mo] (I) that crystallizes (Faller, Chodosh & Katahira, 1980). To establish if a similar correspondence exists between major solution isomer and that observed in the solid state when R = Me, we have determined the crystal structure of [(η^5-C$_5$H$_5$)(2-Me-η^3-C$_3$H$_4$)(CO)$_2$Mo] (II).

Experimental. Yellow crystals, prepared according to the literature (Faller, Chen, Mattina & Jakubowski, 1973), $0 \cdot 05 \times 0 \cdot 04 \times 0 \cdot 03$ cm, from diethyl ether/n-heptane (1:1) by slow evaporation, mounted in Lindemann tube under N$_2$; preliminary unit cell and space group from oscillation and Weissenberg photography [λ(Cu $K\alpha$) = $1 \cdot 54178$ Å], $h0l$ $h+l = 2n+1$ and $0k0$

$k = 2n+1$ absent; CAD-4 diffractometer, 188 K (ULT-1 apparatus), 25 reflections ($17° < \theta < 18°$) centred, graphite-monochromated Mo $K\alpha$ radiation; for data collection $\theta_{max} = 30°$, ω–2θ scans in 96 steps, ω scan width $0 \cdot 8° + 0 \cdot 35°$ tan θ, rapid prescan after which reflections with $I \geq 0 \cdot 5\sigma(I)$ remeasured such that final net intensity had $I > 33\sigma(I)$ subject to a maximum measuring time of 90 s; two quadrants measured ($hk\pm l$ and $-h-k\pm l$) over 115 X-ray hours with no detectable decay or movement; data not corrected for absorption, observed structure factors determined and merged to give 3083 unique reflections, $R_{merg} = 0 \cdot 0218$; for structure solution and refinement 2867 amplitudes for which $F \geq 2\sigma(F)$, Patterson synthesis (Mo), full-matrix least squares (on F) (Sheldrick, 1976), $w = [\sigma^2(F) + 0 \cdot 004524 \, (F)^2]^{-1}$, anisotropic thermal parameters for all non-H atoms, U_H^* set at $0 \cdot 04$ Å^2, $R = 0 \cdot 0250$, $wR = 0 \cdot 0469$, data: variable ratio 17:1, $(\Delta/\sigma)_{max}$ in final cycle $<0 \cdot 3$, max. peak and min. trough in final ΔF synthesis $0 \cdot 41$ and $-1 \cdot 08$ e Å^{-3} respectively, neutral scattering factors for C, O, Mo (Cromer & Liberman, 1970) and H (Stewart, Davidson & Simpson, 1965), computer programs SHELX76 (Sheldrick, 1976), XANADU (Roberts & Sheldrick, 1976), XRAY76 (Stewart, Machin, Dickinson, Ammon, Heck & Flack, 1976), and ORTEPII (Johnson, 1976).†

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* The isotropic temperature factor is defined as exp$[-8\pi^2 U \times (\sin^2\theta)/\lambda^2]$.

† Lists of structure factors, H-atom coordinates, Tables 3 and 4, and anisotropic thermal parameters have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 39027 (22 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.