

# The Crystal and Molecular Structure of Di- $\mu$ -thio-n-butyl(bis- $\pi$ -cyclopentadienylmolybdenum)-iron-dichloride, a Model Compound of the Nitrogenase System

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(Received 14 April 1971)

The crystal and molecular structure of di- $\mu$ -thio-n-butyl(bis- $\pi$ -cyclopentadienylmolybdenum)iron-dichloride, a model compound of the nitrogenase system (monoclinic,  $a = 8.483$ ,  $b = 19.686$ ,  $c = 14.504$  Å,  $\gamma = 116.7^\circ$ ,  $P2_1/b$ ,  $Z = 4$ ) has been determined by three-dimensional X-ray methods from 1835 independent reflexions measured on a linear diffractometer. The structure was refined by full-matrix least-squares  $R = 7.0\%$ .) The iron-molybdenum separation in the bent sulphur bridge is 3.660 Å and there is no metal-metal bond. The FeS<sub>2</sub> and MoS<sub>2</sub> planes are inclined at 148°, Mo-S(mean) is 2.464 and Fe-S(mean) is 2.386 Å. The  $\pi$ -cyclopentadienyl rings are staggered and are inclined at an angle of 133°. The iron atom is approximately tetrahedral and Fe-Cl(mean) is 2.238 Å.

## Introduction

Recent investigations suggest that sulphur-bridged molybdenum-iron systems are a significant feature of nitrogenase enzymes (Spence 1969). The crystal and molecular structure of the model compound di- $\mu$ -thio-n-butyl(bis- $\pi$ -cyclopentadienylmolybdenum)iron-dichloride(I) has been investigated to determine the nature of the Mo...Fe interaction. A preliminary report of this work has been published (Cameron & Prout 1971).

## Experimental

The crystals were prepared by the method of Dias & Green (1969).

### Crystal data

C<sub>18</sub>H<sub>28</sub>Cl<sub>2</sub>FeMoS<sub>2</sub>,  $M = 531.4$ ,

monoclinic,

$a = 8.483 \pm 0.005$  Å,

$b = 19.686 \pm 0.010$  Å,

$c = 14.504 \pm 0.008$  Å,

$\gamma = 116.7 \pm 0.1^\circ$ ,

$U = 2159.8$  Å<sup>3</sup>,

$D_m = 1.61$ ,  $Z = 4$ ,  $D_c = 1.628$  g.cm<sup>-3</sup>,

Space group  $P2_1/b$  ( $C_{2h}^5$ , No. 14).

Mo  $K\alpha$  radiation,  $\mu = 10.32$  cm<sup>-1</sup>.

The unit-cell dimensions and 1835 independent reflexions with intensities greater than  $3\sigma$  were measured with a Hilger and Watts linear diffractometer from a crystal mounted about the  $c$  axis ( $hk0-hk15$ ). The crystal was sealed in a glass capillary. The data were corrected for Lorentz and polarization effects but not for absorption.

From an unsharpened three-dimensional Patterson synthesis, possible positions were assigned to the iron and molybdenum atoms. A Fourier synthesis with phases based upon the positions of these two atoms clearly showed the cyclopentadienyl groups, and the sulphur and chlorine atoms. A difference Fourier synthesis phased upon the positions of these atoms indicated the locations of the  $\alpha$ -carbon atoms of the n-butyl groups, but details of the rest of the fragment were diffuse and uncertain. Chemically reasonable positions that were not inconsistent with the difference synthesis were assigned to the remaining n-butyl carbon atoms and the structure was refined by full-matrix least-squares with isotropic temperature factors on all atoms. After four cycles the isotropic refine-

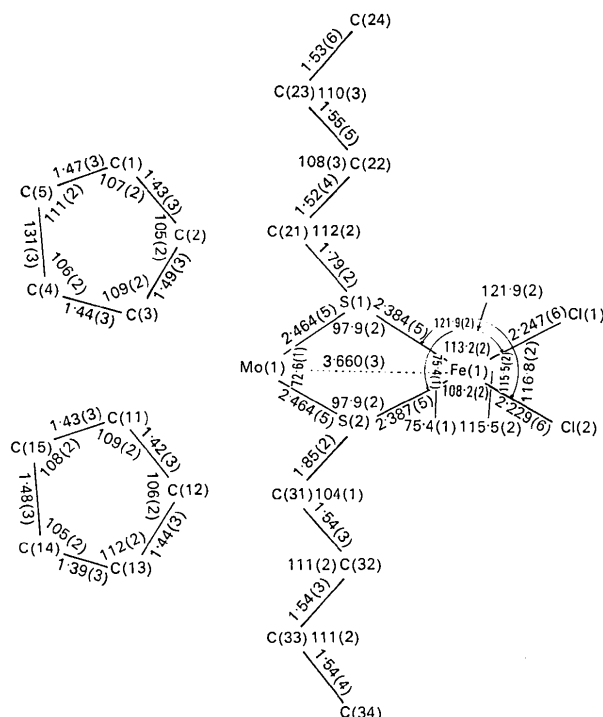


Fig. 1. Interatomic distances and interbond angles with standard deviations in parentheses.

ment converged at  $R=11.0\%$ , and after a further three cycles with anisotropic temperature factors at  $R=7.0\%$ . During the last two cycles the positions of the carbon atoms of the n-butyl groups were constrained to a chemically reasonable configuration by the method of Waser (1963) as implemented in Oxford by Ford and Rollett (Rollett 1970). During the refinement the weighting scheme was

$$w = \{[(50|F_o| - 2400)/2000]^2\}^{-1}.$$

Table 1 lists the observed structure amplitudes and the structure factors calculated from the atomic parameters in Table 2. The atomic scattering factors were

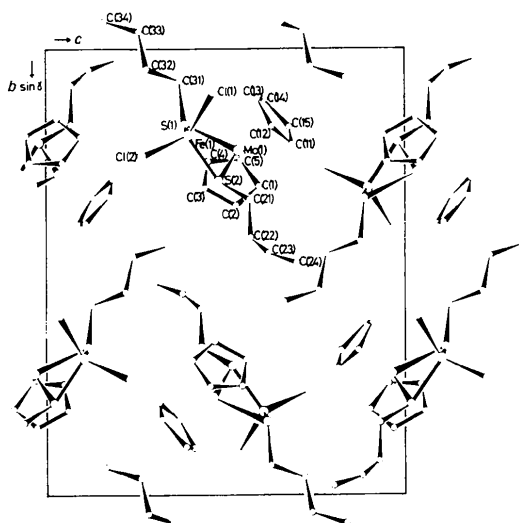
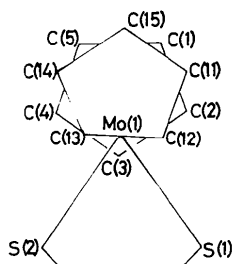
taken from those listed by Cromer & Waber (1965) and those for neutral iron and molybdenum were corrected from the real part of the anomalous dispersion effect. Fig. 1 shows the interatomic distances and interbond angles with their standard deviations. Fig. 2 gives the crystal structure projected down  $a$  and Fig. 3 gives the projection of the  $\pi$ -cyclopentadienyl ligands onto the  $MoS_2$  plane.

### Discussion

The crystals were found to contain isolated units of di- $\mu$ -thio-n-butyl(bis- $\pi$ -cyclopentadienyl)molybdenum) iron dichloride(1) (Fig. 2) with some uncertainty in the

Table 1. *Observed structure amplitudes and calculated structure factors*

l	F <sub>o</sub>	The format is	
		h	k
1	5 F <sub>o</sub>	5	5F <sub>c</sub>
2	10	10	10
3	15	15	15
4	20	20	20
5	25	25	25
6	30	30	30
7	35	35	35
8	40	40	40
9	45	45	45
10	50	50	50
11	55	55	55
12	60	60	60
13	65	65	65
14	70	70	70
15	75	75	75
16	80	80	80
17	85	85	85
18	90	90	90
19	95	95	95
20	100	100	100
21	105	105	105
22	110	110	110
23	115	115	115
24	120	120	120
25	125	125	125
26	130	130	130
27	135	135	135
28	140	140	140
29	145	145	145
30	150	150	150
31	155	155	155
32	160	160	160
33	165	165	165
34	170	170	170
35	175	175	175
36	180	180	180
37	185	185	185
38	190	190	190
39	195	195	195
40	200	200	200
41	205	205	205
42	210	210	210
43	215	215	215
44	220	220	220
45	225	225	225
46	230	230	230
47	235	235	235
48	240	240	240
49	245	245	245
50	250	250	250
51	255	255	255
52	260	260	260
53	265	265	265
54	270	270	270
55	275	275	275
56	280	280	280
57	285	285	285
58	290	290	290
59	295	295	295
60	300	300	300
61	305	305	305
62	310	310	310
63	315	315	315
64	320	320	320
65	325	325	325
66	330	330	330
67	335	335	335
68	340	340	340
69	345	345	345
70	350	350	350
71	355	355	355
72	360	360	360
73	365	365	365
74	370	370	370
75	375	375	375
76	380	380	380
77	385	385	385
78	390	390	390
79	395	395	395
80	400	400	400
81	405	405	405
82	410	410	410
83	415	415	415
84	420	420	420
85	425	425	425
86	430	430	430
87	435	435	435
88	440	440	440
89	445	445	445
90	450	450	450
91	455	455	455
92	460	460	460
93	465	465	465
94	470	470	470
95	475	475	475
96	480	480	480
97	485	485	485
98	490	490	490
99	495	495	495
100	500	500	500

Fig. 2. The crystal structure projected down *a*.Fig. 3. The  $\pi$ -cyclopentadienyl ligands seen in projection onto the  $\text{MoS}_2$  plane.

positions of the terminal groups of the butyl groups. The iron and molybdenum atoms, 3.660 Å apart, are bridged by two S(*n*-butyl) groups. The mean length of the molybdenum-sulphur bonds is 2.464 Å and of the iron-sulphur bonds 2.386 Å. The angle between the  $\text{FeS}_2$  and  $\text{MoS}_2$  planes is 148°. The *n*-butyl groups have the *cis* configuration with respect to the  $\text{FeS}_2\text{Mo}$  system with both  $\alpha$ -carbon atoms on the same side of the  $\text{MoS}_2$  plane as the iron atom. The coordination polyhedron of the molybdenum atom is completed by two  $\pi$ -cyclopentadienyl groups which are in the staggered configuration (Fig. 3) and inclined with respect to one another at an angle of 133°. The environment of the iron atom is approximately tetrahedral with a mean iron-chlorine bond length of 2.238 Å.

When the compound was first prepared there was considerable speculation about a possible iron molybdenum bond. The  $(\pi\text{-C}_5\text{H}_5)_2\text{MoS}_2$  fragment has a pair of *d*-electrons which, according to Ballhausen & Dahl (1961) should occupy an orbital directed between the bridging sulphur atoms towards the iron atom. These electrons could in principle form a donor bond with the iron atom. Alcock (1969), however, places the electron pair in an orbital outside the bridge. On this model metal-metal bonding would not be expected. The molybdenum-iron distance, 3.660 Å, is at first sight too long for a metal-metal bond but it is significantly shorter than the Mo-Rh distance, 3.88 Å, (Prout & Rees, 1971) in  $[(\pi\text{-C}_5\text{H}_5)_2\text{Mo}(\text{SCH}_3)_2\text{Rh}(\pi\text{-C}_3\text{H}_5)_2]^+$ , which contains a planar  $\text{MoS}_2\text{Rh}$  system and significantly shorter than the W-Cr distance, 3.93 Å, in  $(\pi\text{-C}_5\text{H}_5)_2\text{W}(\text{SC}_6\text{H}_5)_2\text{Cr}(\text{CO})_4$  (Cameron *et al.*, 1971),

Table 2. Atomic parameters ( $\times 10^4$ ) with standard deviations ( $\times 10^4$ ) in parentheses

The temperature factor *T* has the form

$$T = \exp[-2\pi^2(U_{11}h^2a^*2 + U_{22}k^2b^*2 + U_{33}l^2c^*2 + 2U_{23}klb^*c^* + 2U_{13}hla^*c^* + 2U_{12}hka^*b^*)].$$

	<i>x/a</i>	<i>y/b</i>	<i>z/c</i>	<i>U</i> <sub>11</sub>	<i>U</i> <sub>22</sub>	<i>U</i> <sub>33</sub>	2 <i>U</i> <sub>23</sub>	2 <i>U</i> <sub>13</sub>	2 <i>U</i> <sub>12</sub>
Mo(1)	307 (2)	2738 (1)	364 (1)	646 (1)	434 (1)	522 (1)	41 (1)	23 (2)	532 (1)
S(1)	-158 (5)	1691 (2)	3875 (3)	616 (2)	452 (2)	548 (2)	-54 (4)	-50 (4)	407 (4)
S(2)	2755 (5)	2936 (2)	4809 (3)	596 (2)	487 (2)	697 (3)	-106 (4)	-122 (4)	361 (3)
Fe(1)	2839 (3)	1912 (1)	3965 (2)	625 (1)	511 (1)	625 (2)	30 (2)	21 (2)	508 (2)
Cl(1)	3172 (6)	968 (2)	4669 (4)	923 (3)	580 (2)	1040 (4)	308 (5)	82 (6)	792 (5)
Cl(2)	4496 (6)	2391 (3)	2713 (4)	824 (3)	1019 (4)	662 (4)	126 (6)	87 (5)	776 (6)
C(1)	-1430 (23)	3070 (9)	5948 (15)	729 (11)	621 (10)	1097 (16)	49 (20)	111 (22)	983 (19)
C(2)	-50 (25)	3491 (9)	5316 (16)	1080 (14)	632 (10)	1082 (16)	32 (22)	40 (27)	1335 (21)
C(3)	-676 (24)	3102 (9)	4413 (12)	1019 (13)	636 (10)	734 (14)	-158 (17)	-323 (20)	1265 (20)
C(4)	-2403 (22)	2484 (10)	4536 (14)	723 (11)	949 (13)	836 (14)	-37 (22)	-80 (22)	1127 (21)
C(5)	-2861 (23)	2463 (11)	5428 (18)	707 (12)	1018 (15)	1319 (20)	-343 (28)	-134 (27)	1168 (23)
C(11)	461 (27)	2120 (10)	6867 (12)	1207 (16)	811 (12)	558 (12)	403 (20)	264 (23)	1154 (24)
C(12)	1148 (24)	1720 (8)	6306 (12)	1069 (14)	468 (9)	576 (12)	122 (15)	-214 (20)	644 (19)
C(13)	-366 (24)	1103 (8)	5892 (12)	1036 (13)	518 (9)	527 (11)	260 (19)	-224 (15)	793 (19)
C(14)	-1925 (24)	1131 (9)	6112 (14)	918 (13)	661 (11)	728 (13)	576 (19)	441 (22)	649 (20)
C(15)	-1413 (28)	1752 (10)	6794 (14)	1231 (16)	705 (12)	664 (13)	400 (20)	630 (24)	881 (23)
C(21)	4398 (26)	3357 (10)	5682 (15)	1104 (16)	893 (14)	1115 (20)	-507 (25)	-1080 (28)	571 (25)
C(22)	5101 (43)	4219 (11)	5699 (28)	2319 (39)	1660 (30)	2845 (55)	-1615 (63)	-3744 (81)	104 (54)
C(23)	6927 (29)	4561 (13)	6193 (25)	2056 (36)	1562 (29)	2557 (52)	-362 (60)	-1277 (73)	1565 (53)
C(24)	6916 (50)	5070 (26)	6984 (27)	2600 (50)	3331 (60)	3011 (77)	-924 (96)	848 (92)	3673 (77)
C(31)	-1898 (21)	707 (7)	3738 (11)	1014 (14)	507 (9)	801 (14)	-334 (18)	-354 (22)	289 (19)
C(32)	-1486 (25)	447 (8)	2805 (12)	1259 (17)	525 (11)	942 (17)	-522 (20)	-279 (26)	280 (22)
C(33)	-2816 (28)	-380 (8)	2596 (14)	1644 (22)	552 (12)	1365 (22)	-335 (26)	-353 (38)	671 (27)
C(34)	-2472 (41)	-618 (12)	1637 (17)	2134 (33)	935 (18)	1991 (36)	-1188 (41)	1026 (55)	538 (31)

where the angle between the  $WS_2$  and  $CrS_2$  planes is  $154.5^\circ$ . The present work is, however, the first report of a sulphur-bridged molybdenum-iron system, so there is no direct comparison for the distance between the molybdenum and iron atoms. Several structures have been reported that contain sulphur bridged iron-iron systems and for those where there is a metal-metal bond the Fe-Fe distances found are  $2.51 \text{ \AA}$  [ $\mu, \mu'$ (*cis*-stilbene- $\alpha, \beta$ -dithiolato-bis(tricarbonyliron))] (Weber & Bryan, 1967),  $2.54 \text{ \AA}$  (ethylthio-irontricarboxyl dimer) (Dahl & Wei, 1963) and di(methylthio-di-ironhexacarbonyl)sulphide (Coleman, Wajcicki, Pollick & Dahl, 1967) and  $2.61 \text{ \AA}$  [bis( $\mu$ -ethylmercaptide- $\mu$ -ethylthioxanthate)di(iron ethyl thioxanthate) (Coucouvani, Lippard & Zubieta, 1969)]. In these compounds the Fe-S bond lengths are in the range  $2.22$ – $2.28 \text{ \AA}$ . In the structure of di- $\mu$ -phenylthiobis( $\pi$ -cyclopentadienyl carbonyl)iron (Ferguson, Hanaway & Islam, 1968), which has many similarities with the present structure, the Fe-Fe distance is  $3.39 \text{ \AA}$ , the Fe-S distance is  $2.26 \text{ \AA}$  (mean) and the two  $FeS_2$  planes are inclined at an angle of  $164^\circ$ . The magnetic properties of this compound confirm that it does not contain a metal-metal bond. Bis( $\pi$ -cyclopentadienyl)oxomolybdenum sulphide (Stevenson & Dahl, 1967) is one of the few sulphur-bridged molybdenum systems of known structure. The Mo-Mo distance is  $2.89 \text{ \AA}$  and the Mo-S distance is  $2.32 \text{ \AA}$ . The  $MoS_2Mo$  grouping is planar and the magnetic measurements are best explained by the presence of a metal-metal bond. More generally in bridged systems Mo-Mo bonded distances have been reported as short as  $2.11 \text{ \AA}$  [molybdenum(II) acetate, Lawton & Mason (1965)] and as long as  $3.26 \text{ \AA}$  [guaiazulene dimolybdenum hexacarbonyl (Churchill & Bird, 1968) and di- $\mu$ -dimethylphosphidobis(tricarbonyltriethylphosphine)molybdenum (Mais, Owston & Thompson, 1967)] with a wide spread of intermediate values. Dahl, Costello & King (1968) and Dahl, Gil & Felthan (1969) point out that metal-metal distances in ligand-bridged complexes are not valid criteria in themselves of metal-metal bonding unless accompanied by deviations in the interbond angles within the bridge system of the complex. The S-Mo-S ( $72.6^\circ$ ) S-Fe-S ( $75.4^\circ$ ) angles are both less than  $80^\circ$  and the Fe-S-Mo angle is  $97.9^\circ$  (mean). In non-bridged systems, the S-Mo-S angle is  $82.4^\circ$  in bis- $\pi$ -cyclopentadienyl(toluene 3-4 dithiolato)molybdenum (Knox & Prout, 1969a), the S-Mo-N angle is  $78.4^\circ$  in bis- $\pi$ -cyclopentadienyl(2-aminoethanethiolato)molybdenum and the Cl-Mo-Cl angle is  $81.5^\circ$  in (bis- $\pi$ -cyclopentadienyl)molybdenum dichloride (Cameron, Prout & Rees, 1971). The S-Mo-S angle in the present work is therefore more acute than is expected which suggests a metal-metal repulsion. The angle at the sulphur atom of a thioalkane bridged system where metal-metal bonding is known to occur is  $83^\circ$  in  $C_5H_5Ti(SMe)_2Mo(CO)_4$  (Davies & Kilbourn, 1971) and in bis( $\pi$ -cyclopentadienyl)oxomolybdenum sulphide (Stevenson & Dahl, 1967) the mean angle at the sulphur atom is  $77.3^\circ$ . Consequently there appears

to be *no evidence* of any type to support the suggestion of a metal-metal bond in  $(\pi-C_5H_5)Mo[S(n-C_4H_9)]_2FeCl_2$ .

The relatively shorter Mo-Fe distance can be attributed to the deformation of the bridging system and to the short metal-sulphur bonds. In particular the Fe-S ( $2.384 \text{ \AA}$ ) bond is markedly shorter than Cr-S ( $2.49 \text{ \AA}$ ) in  $(\pi-C_5H_5)_2W\mu(SC_6H_5)_2Cr(CO)_4$  (Cameron *et al.*, 1971). Molybdenum-sulphur bond lengths in the range  $2.32$ – $2.80 \text{ \AA}$  have been reported, but those to the  $(\pi-C_5H_5)_2Mo$  group lie within a much narrower range,  $2.43 \text{ \AA}$  in bis- $\pi$ -cyclopentadienylmolybdenum toluenedithiolate (Knox & Prout, 1969a),  $2.44 \text{ \AA}$ , in bis- $\pi$ -cyclopentadienyl-(2-aminoethanethiolato)molybdenum iodide (Knox & Prout, 1969b) and  $2.52 \text{ \AA}$  in  $[(\pi-C_5H_5)_2Mo-\mu(SMe)_2Rh(\pi-C_3H_5)_2]^+$  (Prout & Rees, 1971). The deformation of the bridging system is thought to be caused by repulsions between the sulphur lone pair of electrons and the electrons of the Fe-Cl and  $(\pi-C_5H_5)$ -Mo bonds. The tetrahedral environment of the iron atom permits this deformation without serious steric hindrances between the chlorine atoms and the  $\pi$ -cyclopentadienyl group that is on the opposite side of the molecule to the sulphur lone pair electrons.

The Cl-Fe-Cl angle of  $115.5^\circ$  and the S-Fe-S angle of  $75.4^\circ$  are considerably distorted from the tetrahedral angle of  $109.5^\circ$ ; deformation of the tetrahedral environment of iron is not uncommon. Edwards, Johnson & Williams (1967) have shown from Mössbauer effect spectra and magnetic data that in the series of compounds  $A_2FeX_4$  where A is a large cation and X = Cl, Br and NCS, the iron coordination shows large deviations from cubic symmetry.

The  $(\pi-C_5H_5)_2Mo$  group is not significantly different from those reported by Knox & Prout (1969a, b).

We thank the Science Research Council for a fellowship for T.S.C.

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## The Crystal Structure of (–)<sub>589</sub>-*cis*-α-Dinitro-(L-3,8-dimethyltriethylenetetramine)-cobalt(III) Perchlorate, *cis*-α-[Co(NO<sub>2</sub>)<sub>2</sub>(L-3,8-dimetrien)]ClO<sub>4</sub>

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(Received 26 April 1971)

The structure of (–)<sub>589</sub>-*cis*-α-[Co(NO<sub>2</sub>)<sub>2</sub>(L-3,8-dimetrien)]ClO<sub>4</sub> has been determined from the three-dimensional X-ray data collected by the diffractometer method. The compound forms orthorhombic crystals with  $a = 12.395$ ,  $b = 16.829$ ,  $c = 7.864$  Å and  $Z = 4$ , in space group  $P2_12_12_1$ . The structure has been refined by least-squares methods with anisotropic temperature factors to an  $R$  value of 0.056 for 2268 observed reflexions. The perchlorate anion is disordered over two positions. Six nitrogen atoms of the dimetrien ligand and nitro groups are bonded nearly octahedrally to the central cobalt atom. The complex cation has approximately the symmetry 2 ( $C_2$ ). The average Co–N(dimetrien) distance is 1.958 (7) Å, and the average NCoN angle of terminal chelate rings is 86.1 (3)°, whereas that of the central ring is 87.6 (3)°. The complex cation has the absolute configuration  $A$ , and the conformations of the three chelate rings are  $\delta$ ,  $\lambda$  and  $\delta$ , the two methyl groups being in equatorial positions with respect to the chelate rings. The absolute configurations of the two asymmetric nitrogen atoms are both  $S$ .

### Introduction

Three possible isomers of disubstituted triethylenetetraminecobalt(III) complexes (*cis*-α, *cis*-β and *trans*) were recently prepared and isolated as perchlorates by using the stereoselective quadridentate ligand, L-3,8-dimethyltriethylenetetramine:

$H_2NCH_2CH(CH_3)NHCH_2CH_2NHCH(CH_3)CH_2NH_2$ , 3,8-dimetrien (Yoshikawa, Saburi, Sawai & Goto, 1969). The structure of the *cis*-β isomer has already been determined (Ito, Marumo & Saito, 1970). The authors' interest lay in the comparison of the strain energies of the three isomers. Dwyer & Maxwell (1970) have determined the structure of racemic *cis*-α-(amminechlorotriethylenetetramine)cobalt(III) nitrate. From the result large non-bonded interactions between the chelate rings are also expected for L-3,8-dimetrien coordinated in *cis*-α configuration. The crystal structure of (–)<sub>589</sub>-*cis*-α-[Co(NO<sub>2</sub>)<sub>2</sub>(L-3,8-dimetrien)]ClO<sub>4</sub> has been determined in order to establish the stereochemical con-

figuration of the complex cation. The calculation of the strain energy will be reported in the next paper together with that of the *cis*-β and *trans* isomers (Ito, Marumo & Saito, 1972).

### Experimental

The specimens were kindly supplied by Professor S. Yoshikawa of this University. They are orange prismatic crystals elongated along the  $c$  axis, and belong to the orthorhombic system. The cell dimensions,  $a = 12.395 \pm 0.002$ ,  $b = 16.829 \pm 0.002$  and  $c = 7.864 \pm 0.002$  Å, were determined by using a single-crystal diffractometer with Mo  $K\alpha$  radiation ( $\alpha_1 = 0.70926$ ,  $\alpha_2 = 0.71354$  Å). The systematic absences indicate that the space group is  $P2_12_12_1$ . There are four formula units of  $C_8H_{22}ClCoN_6O_8$  in the unit cell ( $D_x = 1.72$  g.cm<sup>-3</sup>,  $D_m = 1.72$  g.cm<sup>-3</sup>). The crystals were reformed into a sphere with a diameter of about 0.22 mm. The intensity data were collected on a Rigaku automatic four-