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## Structural and Strain-Energy-Minimization Study of the Geometric and Configurational Isomers of Bis(L-methioninato)cobalt(III)

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### Abstract

The crystal structures of the three geometric isomers of bis(L-methioninato)cobalt(III) have been determined by

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X-ray analysis. (1) *trans*-S-[Co<sup>III</sup>(L-met)<sub>2</sub>]<sup>+</sup>: Na-[Co(C<sub>5</sub>H<sub>10</sub>NO<sub>2</sub>S)<sub>2</sub>](ClO<sub>4</sub>)<sub>2</sub>, *M<sub>r</sub>* = 577.2, orthorhombic, *P*2<sub>2</sub>1<sub>2</sub>1, *a* = 5.4951 (5), *b* = 11.1890 (9), *c* = 16.604 (2) Å, *V* = 1020.9 (2) Å<sup>3</sup>, *Z* = 2, *D<sub>x</sub>* =

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1.883 g cm<sup>-3</sup>, Mo K $\alpha$ ,  $\lambda = 0.71069 \text{ \AA}$ ,  $\mu = 13.24 \text{ cm}^{-1}$ ,  $F(000) = 588$ ,  $T = 294 \text{ K}$ , final  $R = 0.025$  for 947 reflections. (2) *trans*-N-[Co<sup>III</sup>(L-met)<sub>2</sub>]<sup>+</sup>: [Co(C<sub>5</sub>H<sub>10</sub>NO<sub>2</sub>S)<sub>2</sub>]Cl,  $M_r = 390.8$ , orthorhombic,  $P2_12_12$ ,  $a = 8.525(4)$ ,  $b = 9.381(2)$ ,  $c = 10.225(4) \text{ \AA}$ ,  $V = 817.8(6) \text{ \AA}^3$ ,  $Z = 2$ ,  $D_x = 1.587 \text{ g cm}^{-3}$ , Mo K $\alpha$ ,  $\lambda = 0.71069 \text{ \AA}$ ,  $\mu = 14.25 \text{ cm}^{-1}$ ,  $F(000) = 404$ ,  $T = 294 \text{ K}$ , final  $R = 0.029$  for 754 reflections. (3) *trans*-O-[Co<sup>III</sup>(L-met)<sub>2</sub>]<sup>+</sup>: [Co(C<sub>5</sub>H<sub>10</sub>NO<sub>2</sub>S)<sub>2</sub>]ClO<sub>4</sub>·H<sub>2</sub>O,  $M_r = 472.8$ , orthorhombic,  $P2_12_12$ ,  $a = 8.320(2)$ ,  $b = 10.062(2)$ ,  $c = 21.495(2) \text{ \AA}$ ,  $V = 1799.5(5) \text{ \AA}^3$ ,  $Z = 4$ ,  $D_x = 1.745 \text{ g cm}^{-3}$ , Mo K $\alpha$ ,  $\lambda = 0.71069 \text{ \AA}$ ,  $\mu = 13.7 \text{ cm}^{-1}$ ,  $F(000) = 976$ ,  $T = 294 \text{ K}$ , final  $R = 0.028$  for 1556 reflections. In all three complexes the methioninato ligands coordinate *via* S, N and O donor atoms with a *trans* arrangement of the S atoms in (1), of the N atoms in (2) and of the O atoms in (3). The Co–N and Co–O bond lengths are similar in the three structures and are in the range reported previously for such bonds. The Co–S bond lengths range from 2.245 (1)  $\text{ \AA}$  in (2), 2.261 (2) and 2.275 (2)  $\text{ \AA}$  in (3) to 2.301 (1)  $\text{ \AA}$  in (1), the latter being the longest distance reported for a Co<sup>III</sup>–S(sulfide) bond. The six-membered chelate rings adopt chair conformations in all cases except (3) where one of these rings is disordered over chair and boat conformations. Strain-energy-minimization modelling was employed to investigate steric influences on the conformational, configurational and geometric isomer preferences. The three geometric isomers have similar strain energies.

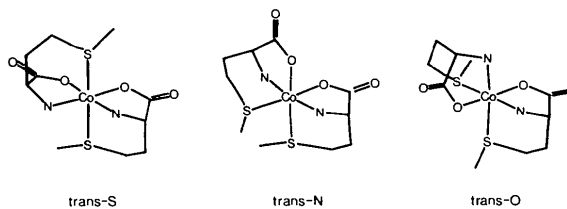
### Introduction

The study of protein structure and conformation by force-field methods, such as strain-energy minimization and molecular dynamics, is an area of developing interest (Karplus & McCammon, 1981, and references therein). However, such studies have rarely been reported for metalloproteins. The reason for this lies, at least in part, in the current lack of adequate force-field parameters for modelling the interaction of metals with proteins. These parameters can only be reliably developed by first modelling low-molecular-weight metal complexes of protein fragments for which precise structural data are available. Also, since development of molecular-mechanics force fields is a semi-empirical process, it is important that this process be undertaken in a stepwise fashion, introducing as few unknowns as possible at each stage. The best developed force fields for metal complexes are those for modelling cobalt(III) complexes (Brubaker & Johnson, 1984) and, therefore, a logical starting point in developing the force fields alluded to above would be to model amino-acid complexes of cobalt(III).

The majority of interactions between transition metals and proteins involve coordinate bonds to thiol sulfur of cysteine residues, sulfide sulfur of methionine

residues and imidazole nitrogen of histidine residues. Therefore, modelling complexes of amino acids such as glycine and alanine, which make up the bulk of structurally characterized species, would not be as useful as modelling complexes containing the aforementioned amino acids.

A particularly attractive set of compounds for modelling is the set of three isomers of bis(L-methioninato)cobalt(III), [Co(L-met)<sub>2</sub>]<sup>+</sup>. The preparation and separation of the geometric isomers of this complex, designated *trans*-S, *trans*-N and *trans*-O (see below), have been reported previously (Hidaka, Yamada & Shimura, 1974). They are relatively stable and can be crystallized separately. In addition to the geometric isomerism, configurational isomerism is possible since coordination of the S atom leads to chirality at that centre. NMR studies indicate that different configurations at S are preferred for each of the geometric isomers (Hidaka *et al.*, 1974). Molecular-mechanics modelling of a series of related isomers provides a better test of a force field since information on both structure and preference for a given geometry is available. Also, since such modelling gives insight into the relative stabilities of the isomers and into structural features it is possible to delineate steric and electronic influences on these properties. Additionally, this set of isomers of a ligand with an S(sulfide) donor atom is of intrinsic interest since unusual isomeric properties have been observed for a number of other cobalt(III) complexes with sulfide moieties (Searle & Larsen, 1976; Gahan, Lawrance & Sargeson, 1982).



We have determined precisely the structures of the three geometric isomers of [Co(L-met)<sub>2</sub>]<sup>+</sup> and report them herein along with the molecular-mechanics modelling of the geometric and configurational isomers of the system.

### Experimental

The complexes were prepared and separated as described previously (Hidaka *et al.*, 1974). Crystals of the perchlorate salt of each isomer were obtained by vapour diffusion of ethanol in a water solution of the bromide salt of the complex and NaClO<sub>4</sub>. Those of the *trans*-S and *trans*-O isomer were suitable for X-ray diffraction analysis while those of the *trans*-N isomer had one crystal axis of 92  $\text{ \AA}$  and were considered unsuitable. Therefore, crystals of the chloride salt of the

Table 1. Summary of data-collection and processing parameters

	(1)	(2)	(3)
Crystal habit	Prismatic	Needles	Needles
Dimensions (mm)	0.11 × 0.18 × 0.09	0.20 × 0.09 × 0.04	0.38 × 0.18 × 0.10
Transmission factors	0.90, 0.86	0.95, 0.84	0.86, 0.78
Scan mode	$\omega$ -1.67 $\theta$	$\omega$ -0.67 $\theta$	$\omega$ -1.67 $\theta$
2 $\theta$ range (°)	1.0-50.0	1.0-50.0	1.0-50.0
Intensity standards	Three	Three	Three
Decomposition (%)	< 3	< 3	< 3
Reflections measured	1094	872	1844
Unique reflections	1034	839	1717
$R_{int}$	0.01	0.01	0.01
Range of $hkl$	0-6, 0-13, 0-19	0-10, 0-11, 0-12	0-9, 0-11, 0-25
Reflections used	947	872	1566
$ I > 2.5\sigma(I) $			
$R$	0.025	0.029	0.028
$wR$	0.030	0.036	0.033
Weighting constants $g, k$ [ $w = g/(\sigma^2 F_o + kF_o^2)$ ]	1.09, $1.3 \times 10^{-4}$	1.2, $1.8 \times 10^{-4}$	1.39, $1.6 \times 10^{-4}$
Shift/e.s.d.	0.2	0.1	0.3
Largest peaks ( $e \text{ \AA}^{-3}$ )	+0.4, -0.25	+0.5, -0.4	+0.3, -0.3

*trans*-N isomer were obtained in a manner analogous to that for the perchlorate salts.

Crystals were mounted on glass fibres with cyanoacrylate resin. Cell dimensions were determined by a least-squares fit to the setting parameters of 25 independent reflections in the range  $8 < \theta < 12^\circ$ , measured and refined on an Enraf-Nonius CAD-4F four-circle diffractometer with graphite-monochromated radiation. Details of the data collection and structure refinement are collected in Table 1.

### Structure determination and refinement

The structures were solved by heavy-atom methods and refined by full-matrix least-squares methods. Origins were defined by fixing the  $y$  and  $z$  coordinates of the Co atom to zero in (1) and the  $x$  and  $y$  coordinates of the Co atom to  $\frac{1}{2}$  in (2). The absolute configurations of the structures were established in the early stages of the refinement by ensuring that the methioninato ligands had the expected L configuration. H atoms were fully refined, with individual isotropic thermal parameters, and non-H atoms were all refined anisotropically. The six-membered chelate ring of one of the ligands in the *trans*-O isomer was found to be conformationally disordered. Two sites were observed for atoms C(6) and C(7) of this ligand and they were refined with a complementary occupancy factor which refined to 57 (1):43 (1). H atoms bonded to C(6), C(7), C(6'), C(7') and C(8) were included at sites calculated assuming tetrahedral geometry about the C atom (C-H 0.97 Å). Positional and equivalent isotropic thermal parameters are given in Tables 2, 3 and 4.\*

\* Lists of structure amplitudes, anisotropic thermal parameters of non-H atoms, positional and thermal parameters of H atoms and full bond lengths and angles have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 51061 (31 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Table 2. Positional parameters ( $\times 10^4$ ) for (1)
$$B_{eq} = \frac{8}{3}\pi^2 \sum_i \sum_j U_{ij} a_i^* a_j^* a_i \cdot a_j$$

	$x$	$y$	$z$	$B_{eq}(\text{\AA}^2)$
Co(1)	7060.6 (13)	0	0	1.47
S(1)	7374.1 (21)	-265.0 (9)	-1370.3 (7)	2.25
O(1)	4618 (5)	1179 (3)	-106 (2)	2.07
O(2)	3920 (6)	-3056 (3)	460 (2)	2.84
N(1)	9286 (7)	1356 (3)	-123 (3)	1.80
C(1)	4838 (18)	-1156 (6)	-1715 (4)	4.35
C(2)	6674 (10)	1169 (5)	-1832 (3)	2.53
C(3)	8272 (10)	2138 (4)	-1492 (3)	2.69
C(4)	8002 (8)	2313 (4)	-576 (3)	2.01
C(5)	5324 (8)	2228 (4)	-362 (3)	2.02
Na(1)	6283 (5)	0	5000	2.71
Cl(2)	-1156.4 (22)	4138.9 (11)	1365.1 (7)	2.43
O(3)	-201 (12)	2949 (4)	1377 (4)	4.78
O(4)	-1562 (14)	4486 (8)	2170 (3)	6.07
O(5)	-3476 (12)	4105 (7)	987 (5)	6.46
O(6)	366 (16)	4896 (10)	929 (7)	9.97
O(3')	-2681 (59)	4671 (28)	796 (20)	1.02
O(4')	-664 (75)	4818 (36)	2056 (29)	0.66
O(5')	-1329 (89)	2924 (43)	1143 (27)	2.85
O(6')	951 (82)	4209 (43)	915 (25)	4.29
O(3'')	-1530 (112)	3314 (78)	1928 (48)	7.02
O(4'')	-55 (109)	5038 (75)	1836 (49)	4.82
O(5'')	-3503 (99)	4821 (49)	1156 (33)	2.72
O(6'')	904 (99)	4624 (68)	1206 (31)	3.95

Table 3. Positional parameters ( $\times 10^4$ ) for (2)
$$B_{eq} = \frac{8}{3}\pi^2 \sum_i \sum_j U_{ij} a_i^* a_j^* a_i \cdot a_j$$

	$x$	$y$	$z$	$B_{eq}(\text{\AA}^2)$
Co(1)	5000	5000	6991.5 (7)	1.34
S(1)	5096.0 (21)	3321.9 (11)	8555.2 (11)	2.07
O(1)	4906 (5)	3616 (3)	5640 (3)	1.92
O(2)	6377 (4)	2273 (5)	4361 (4)	3.68
N(1)	7266 (5)	4813 (5)	6829 (4)	1.65
C(1)	3199 (7)	2520 (7)	8678 (8)	3.33
C(2)	6131 (7)	1831 (5)	7815 (6)	2.48
C(3)	7704 (7)	2257 (6)	7222 (6)	2.38
C(4)	7593 (5)	3422 (5)	6203 (5)	1.93
C(5)	6227 (6)	3073 (5)	5294 (5)	2.37
Cl(1)	0	5000	9109.7 (14)	2.35

Programs used were *SUSCAD* (Guss, 1976a) for data reduction, *ABSORB* (Guss, 1976b) for absorption corrections, *SHELX76* (Sheldrick, 1976) for solution and refinement and *ORTEP* (Johnson, 1965) for plotting. Scattering factors and anomalous-dispersion terms were taken from *International Tables for X-ray Crystallography* (1974).

### Molecular mechanics

The strain energy of a molecule was described as the sum over all individual interactions of bond deformation ( $E_b$ ), valence-angle deformation ( $E_\theta$ ), torsion-angle deformation ( $E_\phi$ ), out-of-plane deformation ( $E_\delta$ ) and non-bonded interaction ( $E_{nb}$ ) energies:

$$E_{total} = \sum E_b + \sum E_\theta + \sum E_\phi + \sum E_\delta + \sum E_{nb}$$

The force field was developed from those described previously for hexaamminecobalt(III) and triaminetrisulfidocobalt(III) complexes (Hambley, Hawkins, Palmer & Snow, 1981; Hambley & Snow, 1986).

Table 4. Positional parameters ( $\times 10^4$ ) for (3)
$$B_{eq} = \frac{8}{3}\pi^2 \sum_i \sum_j U_{ij} a_i^* a_j^* a_i \cdot a_j$$

	x	y	z	$B_{eq}(\text{\AA}^2)$
Co(1)	3320.6 (7)	-765.1 (6)	6264.8 (3)	1.92
S(1)	4786.4 (16)	622.6 (13)	5651.2 (6)	2.77
S(2)	4446.1 (18)	-2412.3 (13)	5697.5 (8)	3.51
O(1)	1536 (4)	-666 (3)	5726 (1)	2.48
O(2)	-496 (4)	610 (4)	5439 (2)	3.94
O(3)	5016 (4)	-877 (4)	6853 (2)	2.68
O(4)	5993 (5)	-2142 (4)	7611 (2)	3.36
N(1)	2298 (5)	735 (4)	6686 (2)	2.24
N(2)	2265 (5)	-2072 (4)	6801 (2)	2.56
C(1)	6096 (8)	1598 (7)	6139 (3)	3.85
C(2)	3393 (8)	1857 (5)	5375 (3)	3.50
C(3)	2297 (7)	2455 (5)	5860 (3)	3.09
C(4)	1294 (6)	1437 (5)	6217 (2)	2.36
C(5)	662 (6)	405 (5)	5765 (2)	2.60
C(6)	3629 (15)	-2441 (13)	4987 (5)	4.12
C(6')	2638 (21)	-3285 (15)	5288 (8)	4.90
C(7)	3766 (12)	-3957 (8)	6058 (4)	2.92
C(7')	5179 (18)	-3641 (13)	6120 (7)	3.96
C(8)	4081 (8)	-4037 (6)	6729 (4)	4.02
C(9)	3547 (7)	-2838 (5)	7118 (3)	2.86
C(10)	4948 (6)	-1900 (5)	7222 (2)	2.48
Cl(1)	-1130.3 (23)	-4968.2 (18)	6529.2 (9)	5.04
O(5)	2916 (6)	570 (8)	3018 (2)	8.73
O(6)	3560 (19)	514 (12)	4028 (3)	10.43
O(7)	3946 (22)	-1378 (11)	3407 (10)	14.63
O(8)	5470 (12)	156 (20)	3440 (8)	16.06
O(6')	8329 (65)	-4171 (64)	6926 (21)	7.06
O(7')	7539 (43)	-5079 (37)	5950 (14)	2.67
O(8')	10426 (48)	-5829 (35)	6781 (15)	3.45
O(9')	7573 (69)	-4366 (76)	6010 (26)	5.53
O(10')	7753 (70)	-3609 (59)	6420 (27)	5.53
OW(1)	971 (7)	4370 (8)	7981 (4)	8.13

Extensions were necessary to allow modelling of the coordinated carboxylate moiety. Force constants for cobalt(III) complexes of simple amino acids have been described previously (Buckingham, Maxwell, Sargeson & Snow, 1970) and therefore starting points for the carboxylate force field were available. However, the remainder of the force field employed here had been developed and altered from that used in the earlier studies and modifications along the same line were expected to be necessary. Potential-energy parameters are listed in Table 5.

Strain-energy minimization was achieved using a locally written program (MOMEC87; Hambley, 1987) based on the Newton-Raphson refinement method first described by Boyd (1968). All refinements were continued until shifts in positional parameters were less than 0.001 Å. No symmetry constraints were imposed on the refinements.

### Description of the structures

*trans*-S-[Co(L-met)<sub>2</sub>]<sup>+</sup> (1). The structure consists of [Co(L-met)<sub>2</sub>]<sup>+</sup> and Na<sup>+</sup> cations, both lying on crystallographic twofold rotation axes, and a ClO<sub>4</sub><sup>-</sup> anion, rotationally disordered over three sites. There are two hydrogen bonds, one from each of the H(amine) atoms to O(perchlorate) [N...O, 3.076 (8) Å] and coordinated O(carboxylate) [N...O, 2.937 (7) Å] atoms (Table 6). The Na cation is surrounded by the

Table 5. Force-field parameters for (methioninato)-cobalt(III) complexes

(i) Bond-length deformation,  $E_b = \frac{1}{2}k_r(r-r_0)^2$

	$r_0(\text{\AA})$	$k_r(\text{kJ mol}^{-1} \text{\AA}^{-2})$
Co-N	1.905	1055
Co-O	1.845	1055
Co-S	2.080	361
C-C	1.500	3012
C-N	1.490	3615
C-S	1.820	2410
C-CC*	1.500	3012
CC-O	1.290	4819
CC-OT*	1.220	5422
CC-C	1.500	3012
C-H	0.970	3012
N-H	0.910	3398

(ii) Valence-angle deformation,  $E_\theta = \frac{1}{2}k_\theta(\theta-\theta_0)^2$

	$\theta_0(^{\circ})$	$k_\theta(\text{kJ mol}^{-1} \text{rad}^{-2})$
Co-O-CC	120.0	30
Co-N-C	110.0	120
Co-S-C	95.8	90
C-S-C	94.3	151
S-C-C	107.8	211
S-C-H	108.2	151
C-CC-O	118.4	151
C-CC-OT	118.4	151
O-CC-OT	123.1	151
C-C-N	109.5	271
CC-C-N	109.5	271
C-C-C	109.5	271
C-C-CC	109.5	271
C-N-C	109.5	271
Co-N-H	109.7	60
C-N-H	109.4	217
N-C-H	109.4	217
C-C-H	109.4	217
CC-C-H	109.4	217
H-N-H	109.0	193
H-C-H	109.0	193

(iii) Torsion-angle deformation,  $F_\omega = \frac{1}{2}k_\omega[1 + n\cos(\varphi + \varphi_{on})]$

	n	$k_\omega(\text{kJ mol}^{-1})$	$\varphi_{on}(^{\circ})$
-C-C-	3	1.02	0
-C-N-	3	0.60	0
-C-S-	3	0.60	0
-C-CC-	6	0.30	30.0
-CC-O-	2	2.41	90.0

(iv) Out-of-plane deformation,  $E_\delta = \frac{1}{2}k_\delta\delta^2$

	$k_\delta(\text{kJ mol}^{-1})$
CC-C(-O)-OT	48

(v) Non-bonded interaction,  $E_{nb} = 602.5[2014(\epsilon_i\epsilon_j)^{1/2} \times \exp(-12.5r_{ij}/\sum r_{vdw}) - 0.0156(\epsilon_i\epsilon_j)^{1/2} \times (\sum r_{vdw}/r_{ij})^6]$

	$\epsilon$	$r_{vdw}(\text{\AA})$
C	0.044	1.90
N	0.052	1.80
O	0.056	1.70
H	0.046	1.50
S	0.185	2.00

\* CC is the *sp*<sup>2</sup> C atom and OT the non-coordinated carboxylate O atom.

non-coordinated O(carboxylate) and two O(perchlorate) atoms at distances of 2.308 (8), 2.463 (9) and 2.404 (9) Å respectively. The twofold symmetry about the Na atom gives rise to a six-coordinate geometry which is close to octahedral.

Table 6. Close intermolecular contacts (Å)

(a) Compound (1)	N...O	H...O
N(1)—HN(1B)...O(3 <sup>i</sup> )	3.076 (8)	2.25 (6)
N(1)—HN(1A)...O(1 <sup>i</sup> )	2.937 (7)	2.23 (5)
Symmetry code: (i) 1+x, y, z.		
(b) Compound (2)	N...X	H...X
N(1)—HN(1B)...O(2 <sup>i</sup> )	2.854 (6)	2.02 (5)
N(1)—HN(1A)...Cl(1 <sup>ii</sup> )	2.937 (3)	2.38 (3)
Symmetry code: (i) $\frac{1}{2}-x, \frac{1}{2}+y, 1-z$ ; (ii) 1+x, y, z.		
(c) Compound (3)	X...O	H...O
N(1)—HN(1A)...O(4 <sup>i</sup> )	2.978 (8)	2.09 (6)
N(1)—HN(1B)...O(6 <sup>ii</sup> )	3.029 (10)	2.46 (10)
N(1)—HN(1B)...OW(1 <sup>iii</sup> )	3.129 (8)	2.51 (6)
N(1)—HN(1B)...O(5 <sup>iii</sup> )	3.187 (8)	2.54 (7)
N(2)—HN(2B)...O(5 <sup>iii</sup> )	3.025 (8)	2.33 (7)
N(2)—HN(2A)...O(7 <sup>iv</sup> )	3.202 (8)	2.49 (7)
N(2)—HN(2B)...OW(1 <sup>iii</sup> )	3.058 (8)	2.31 (6)
OW(1)—HW(1B)...O(4 <sup>i</sup> )	3.212 (7)	2.83 (5)
OW(1)—HW(1A)...O(8 <sup>i</sup> )	3.120 (9)	2.46 (7)
OW(1)—HW(1A)...O(8 <sup>ii</sup> )	2.628 (10)	1.86 (10)
OW(1)—HW(1B)...O(7 <sup>iii</sup> )	3.169 (8)	2.37 (7)
Symmetry code: (i) 1-x, $\frac{1}{2}-y, \frac{3}{2}-z$ ; (ii) -x, $-\frac{1}{2}-y, \frac{3}{2}-z$ ; (iii) $\frac{1}{2}-x, -y, \frac{1}{2}+z$ ; (iv) $\frac{1}{2}, -\frac{1}{2}-y, 1-z$ .		

A view of the complex is shown in Fig. 1. The Co atom is coordinated to two tridentate L-met ligands *via trans*-S(sulfide), *cis*-N(amine) and *cis*-O(carboxylate) atoms giving near-octahedral geometry. The configuration at the S(sulfide) atom is *S*. The five-membered chelate ring adopts an envelope conformation and the six-membered ring a chair conformation. Bond lengths within the L-met ligand are normal and only the Co—S—C angles show evidence of strain, being opened to 107–109° from the more normal values around 100°.

Co—N and Co—O bond lengths are within the range observed previously (Tulip, Cooper, Hambley, Murdoch & Freeman, 1988) but the Co—S

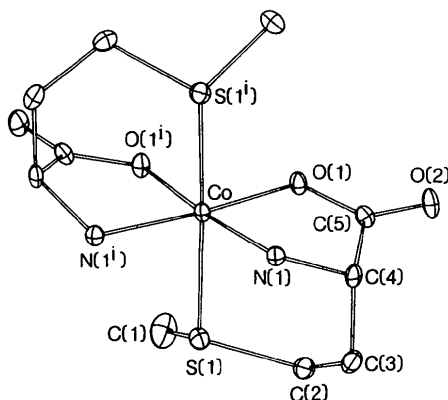


Fig. 1. ORTEP plot of *trans*-S-[Co(L-met)<sub>2</sub>]<sup>+</sup> giving atom numbering.

Table 7. Comparison of crystal structure and energy-minimized bond lengths (Å) and angles (°) for (1)

	Crystal structure	Energy minimized
S(1)—Co(1)	2.301 (1)	2.277
O(1)—Co(1)	1.890 (3)	1.951
N(1)—Co(1)	1.959 (4)	1.881
O(1)—Co(1)—S(1)	92.9 (1)	92.0
N(1)—Co(1)—S(1)	87.1 (1)	86.5
N(1)—Co(1)—O(1)	83.8 (1)	86.1
S(1)—Co(1)—S(1 <sup>i</sup> )	171.4 (1)	177.7
O(1)—Co(1)—O(1 <sup>i</sup> )	89.5 (2)	92.1
N(1)—Co(1)—N(1 <sup>i</sup> )	102.8 (2)	96.0
C(1)—S(1)—Co(1)	109.0 (3)	110.1
C(2)—S(1)—Co(1)	106.7 (2)	106.3
C(2)—S(1)—C(1)	101.0 (3)	100.0
C(5)—O(1)—Co(1)	116.5 (3)	114.4
C(4)—N(1)—Co(1)	108.3 (3)	106.4
C(3)—C(2)—S(1)	110.8 (3)	112.4
C(4)—C(3)—C(2)	113.9 (4)	114.4
C(3)—C(4)—N(1)	111.2 (4)	113.2
C(5)—C(4)—N(1)	107.3 (4)	106.4
C(5)—C(4)—C(3)	108.5 (4)	110.2
C(4)—C(5)—O(1)	114.9 (4)	115.5
O(2)—C(5)—O(1)	122.7 (4)	122.6
O(2)—C(5)—C(4)	122.4 (4)	121.8

bond [at 2.301 (1) Å] is the longest reported for a Co<sup>III</sup>-sulfide complex. It is possible that the unusually long bond is due in part to a *trans* effect but it is longer than those in [Co{(S)-Me-L-cys}<sub>2</sub>]ClO<sub>4</sub>·H<sub>2</sub>O [2.270 (2), 2.273 (2) Å; De Meester & Hodgson, 1976] and [Co(tasn)<sub>2</sub>](CF<sub>3</sub>SO<sub>3</sub>)<sub>3</sub> (tasn = 1-thia-4,7-diazacyclononane) [2.251 (1), 2.246 (1) Å; Hambley, Gahan & Searle, 1988], both of which have *trans*-S arrangements, which suggests that steric factors must also play a role here. Bond lengths and angles for the complex cation are given in Table 7.

*trans*-N-[Co(L-met)<sub>2</sub>]<sup>+</sup> (2). The structure consists of a [Co(L-met)<sub>2</sub>]<sup>+</sup> cation and a Cl<sup>-</sup> anion, both lying on two-fold rotation axes. There are hydrogen bonds from the H(amine) atoms to the non-coordinated O(carboxylate) [N...O, 2.854 (6) Å] and Cl<sup>-</sup> [N...Cl<sup>-</sup>, 2.937 (3) Å] atoms (Table 6).

The arrangement about the Co atom is *trans*-N(amine), *cis*-S(sulfide), *cis*-O(carboxylate). The configuration at the S atom is again *S*. The five- and six-membered chelate rings adopt envelope and chair conformations respectively. Co—N and Co—O bond lengths are normal and the Co—S distance is in the middle of the range reported for such bonds. Bond lengths and angles for the complex are given in Table 8 and a view of the complex cation is shown in Fig. 2.

*trans*-O-[Co(L-met)<sub>2</sub>]<sup>+</sup> (3). The structure consists of a [Co(L-met)<sub>2</sub>]<sup>+</sup> cation, a rotationally disordered perchlorate anion and a single water molecule of hydration. There are numerous hydrogen bonds from H(amine) and H(water) atoms to O(carboxylate), O(perchlorate) and O(water) atoms [N...O, 2.978 (8)–3.202 (8) Å, O...O, 2.628 (10)–3.212 (7) Å] (Table 6).

The arrangement about the Co atom is *trans*-O(carboxylate), *cis*-N(amino), *cis*-S(sulfide). The

Table 8. Comparison of crystal structure and energy-minimized bond lengths (Å) and angles (°) for (2)

	Crystal structure	Energy minimized
S(1)—Co(1)	2.245 (1)	2.250
O(1)—Co(1)	1.898 (3)	1.897
N(1)—Co(1)	1.947 (4)	1.958
O(1)—Co(1)—S(1)	92.3 (1)	94.9
N(1)—Co(1)—S(1)	87.8 (1)	86.9
N(1)—Co(1)—O(1)	85.3 (2)	83.7
S(1)—Co(1)—S(1)	89.2 (1)	88.5
O(1)—Co(1)—O(1)	86.5 (2)	81.8
N(1)—Co(1)—N(1)	170.2 (3)	170.9
C(1)—S(1)—Co(1)	108.2 (2)	110.4
C(2)—S(1)—Co(1)	105.1 (2)	105.3
C(2)—S(1)—C(1)	98.3 (3)	99.9
C(5)—O(1)—Co(1)	115.7 (3)	116.6
C(4)—N(1)—Co(1)	107.7 (3)	107.4
C(3)—C(2)—S(1)	113.0 (4)	112.6
C(4)—C(3)—C(2)	114.1 (4)	114.6
C(3)—C(4)—N(1)	110.5 (4)	113.1
C(5)—C(4)—N(1)	108.0 (4)	106.0
C(5)—C(4)—C(3)	108.2 (4)	110.3
O(2)—C(5)—O(1)	123.4 (5)	123.4
C(4)—C(5)—O(1)	114.6 (4)	114.2
C(4)—C(5)—O(2)	121.9 (5)	122.4

configuration at the S atoms is *R* in each case, opposite to that observed for the *trans-S* and *trans-N* isomers. The C atoms bonded to S(2) are disordered over two sites with occupancies 57 (1):43 (1). This disorder arises from the six-membered chelate ring adopting a boat conformation 57% of the time and a chair conformation 43% of the time. The six-membered ring of the other ligand adopts a chair conformation and both five-membered rings adopt envelope conformations. Views of the complex cation showing boat and chair conformations of the disordered ligand are shown in Figs. 3(a) and 3(b) respectively.

The Co—S bond lengths [2.275 (1), 2.261 (2) Å] are at the long end of the range previously observed {e.g. [Co(azacpten)]ZnCl<sub>4</sub>.Cl (azacpten = 1-methyl-3,13,16-trithia-6,8,10,19-tetraazabicyclo[6.6.6]eicosane, 2.226 (1) Å; Gahan, Hambley, Sargeson & Snow

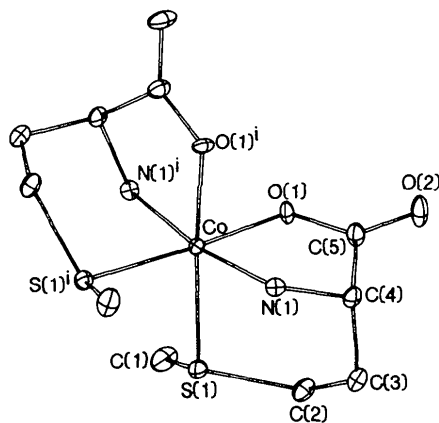


Fig. 2. ORTEP plot of *trans-N*-[Co(L-met)<sub>2</sub>]<sup>+</sup> giving atom numbering.

(1982); [Co(daes)<sub>2</sub>]<sup>3+</sup> [daes = 2,2'-thiobis(ethylamine)], 2.246 (1) Å; Hammershoi, Larsen & Larsen (1978); *cis*- and *trans*-[Co(tasn)<sub>2</sub>]<sup>3+</sup>, 2.217 (2) and 2.251 (1), 2.246 (1) Å; Hambley *et al.* (1988)} but are significantly shorter than the Co—S bond in the *trans-S* complex. Co—N and Co—O bond lengths are again normal. Bond lengths and angles for the complex are listed in Table 9.

### Discussion of molecular mechanics

Strain energies were calculated for each of the three geometric isomers of [Co(L-met)<sub>2</sub>]<sup>3+</sup> (*trans-S*, *trans-N* and *trans-O*) and, for each of these, all combinations of configurations at the S atom were considered *S,S*, *S,R*, *R,R*. For the *trans-O* isomer the boat conformation of one six-membered ring was also considered since this was observed in the crystal structure. The strain-energy-minimized structure of *trans-S*-[Co{(S)-Me-L-cys}<sub>2</sub>]<sup>+</sup> was calculated for comparison with the crystal structure of this cation. Final strain energies are collected in Table 10.

*trans-S*-[Co(L-met)<sub>2</sub>]<sup>+</sup> (1). Comparison of the crystal-structure geometry for this isomer and the strain-

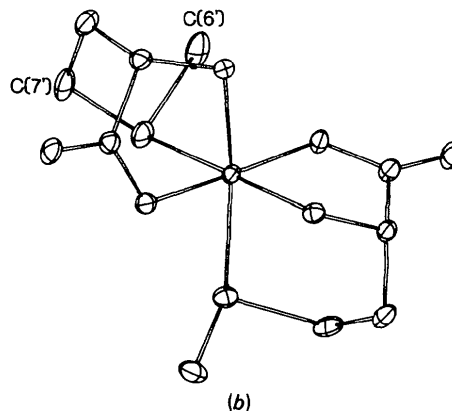
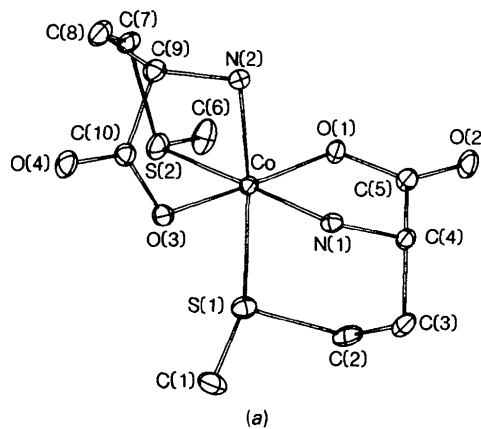


Fig. 3. ORTEP plot of *trans-O*-[Co(L-met)<sub>2</sub>]<sup>+</sup> for (a) the boat and (b) the chair conformation of the second ligand giving atom numbering.

Table 9. Comparison of crystal structure and energy-minimized bond lengths (Å) and angles (°) for (3)

	Crystal structure	Energy minimized
S(1)—Co(1)	2.275 (1)	2.253
S(2)—Co(1)	2.261 (2)	2.253
O(1)—Co(1)	1.886 (3)	1.886
O(3)—Co(1)	1.898 (3)	1.886
N(1)—Co(1)	1.956 (4)	1.958
N(2)—Co(1)	1.956 (4)	1.958
S(2)—Co(1)—S(1)	85.1 (1)	84.6
O(1)—Co(1)—S(1)	91.9 (1)	98.0
O(1)—Co(1)—S(2)	91.9 (1)	90.6
O(3)—Co(1)—S(1)	91.4 (1)	90.6
O(3)—Co(1)—S(2)	90.4 (1)	98.0
O(3)—Co(1)—O(1)	176.1 (1)	168.2
N(1)—Co(1)—S(1)	91.6 (1)	89.2
N(1)—Co(1)—S(2)	175.0 (1)	170.4
N(1)—Co(1)—O(1)	84.3 (2)	83.0
N(1)—Co(1)—O(3)	93.5 (2)	89.3
N(2)—Co(1)—S(1)	174.0 (1)	170.4
N(2)—Co(1)—S(2)	90.6 (1)	89.2
N(2)—Co(1)—O(1)	92.5 (2)	89.3
N(2)—Co(1)—O(3)	84.4 (2)	83.0
N(2)—Co(1)—N(1)	92.9 (2)	97.8
C(1)—S(1)—Co(1)	108.7 (2)	112.6
C(2)—S(1)—Co(1)	105.6 (2)	106.0
C(2)—S(1)—C(1)	101.8 (3)	103.6
C(6)—S(2)—Co(1)	109.7 (4)	112.6
C(6')—S(2)—Co(1)	104.7 (4)	108.2*
C(7)—S(2)—Co(1)	105.4 (3)	106.0
C(7)—S(2)—C(6)	104.3 (6)	103.6
C(7')—S(2)—Co(1)	113.9 (5)	104.4
C(7')—S(2)—C(6')	101.3 (7)	100.7
C(5)—O(1)—Co(1)	116.4 (3)	116.7
C(10)—O(3)—Co(1)	114.9 (3)	116.7
C(4)—N(1)—Co(1)	107.2 (3)	107.0
C(9)—N(2)—Co(1)	107.3 (3)	107.0
C(3)—C(2)—S(1)	115.9 (4)	114.7
C(4)—C(3)—C(2)	114.2 (4)	114.8
C(3)—C(4)—N(1)	110.6 (4)	113.2
C(5)—C(4)—N(1)	107.7 (4)	106.0
C(5)—C(4)—C(3)	109.1 (4)	110.8
O(2)—C(5)—O(1)	123.3 (5)	112.9
C(4)—C(5)—O(1)	114.4 (4)	115.0
C(4)—C(5)—O(2)	122.0 (4)	122.0
C(8)—C(7)—S(2)	114.1 (6)	114.7
C(8)—C(7')—S(2)	114.5 (8)	112.0
C(9)—C(8)—C(7)	116.1 (6)	114.8
C(9)—C(8)—C(7')	113.8 (6)	115.2
C(8)—C(9)—N(2)	111.5 (5)	113.2
C(10)—C(9)—N(2)	107.3 (4)	106.0
C(10)—C(9)—C(8)	110.3 (5)	110.8
O(4)—C(10)—O(3)	122.7 (5)	122.9
C(9)—C(10)—O(3)	115.9 (4)	115.0
C(9)—C(10)—O(4)	121.3 (4)	122.0

\* For primed atoms the comparison is with the energy-minimized chair-boat structure.

energy-minimized geometry (Table 7) shows generally good agreement. The calculated Co—S bond length is 2.277 Å, unusually long, but not as long as that observed in the crystal structure [2.301 (1) Å]. Thus, steric factors do explain at least part of the extension of this bond but there remains the possibility of some electronic *trans* effect. The deformed Co—S—C angles are well reproduced by the molecular-mechanics model. The Co—S(1)—C(2) angle is opened to accommodate the steric requirements of the six-membered chelate ring and the Co—S(1)—C(1) angle is opened to relieve the

Table 10. Minimized strain energies (kJ mol<sup>-1</sup>) for the geometric and configurational isomers of [Co<sup>III</sup>(L-met)<sub>2</sub>]<sup>+</sup>

Isomer	Configuration	$E_b$	$E_{nb}$	$E_\theta$	$E_\phi$	$E_\delta$	$E_{total}$
<i>trans</i> -S	<i>S,S</i>	20.6	47.3	20.8	11.7	0.1	100.5
	<i>R,S</i>	21.0	45.6	24.8	11.7	0.1	103.2
<i>trans</i> -N	<i>R,R</i>	20.9	43.3	28.7	11.9	0.1	104.9
	<i>S,S</i>	19.1	49.0	20.8	9.9	0.1	98.9
<i>trans</i> -O	<i>R,S</i>	18.1	45.1	24.3	10.5	0.1	98.1
	<i>R,R</i>	19.1	46.0	28.1	14.1	0.0	107.2
	<i>S,S</i>	18.4	43.2	28.7	9.0	0.2	99.5
	<i>R,S</i>	19.8	44.8	26.6	8.2	0.2	99.5
	<i>R,R</i>	19.4	46.9	27.0	8.2	0.2	101.6
	<i>S,S</i> *	21.5	52.4	26.7	16.5	0.1	117.2
	<i>R,S</i> *	19.6	45.5	29.8	14.4	0.1	109.4
	<i>R,R</i> *	20.5	48.5	25.7	12.4	0.1	107.2

\* Indicates the second ligand is in the boat conformation.

interaction between the methyl group and the coordinated O atom of the other ligand. In the energy-minimized structure the C(1)—O(1') distance is 2.934 Å corresponding to an interaction energy of 0.87 kJ mol<sup>-1</sup>. The equivalent distance in the crystal structure is 3.025 (8) Å.

The <sup>1</sup>H NMR spectrum of the *trans*-S isomer showed only one sharp signal and this was interpreted as being evidence for the stereoselective formation of only one configuration at S, most likely (*S,S*) (Hidaka *et al.*, 1974). This is confirmed by the calculations which show that the *R,S* and *R,R* configurations are less stable by 3 to 4 kJ mol<sup>-1</sup>. The lower stability of the *R* configurations results from the disposition of the methyl group [C(1)] toward the coordinated NH<sub>2</sub> group rather than toward the sterically less demanding coordinated O atom as in the *S* configuration. Close contacts between these groups [C(1)⋯HN(1B') 2.74 Å, 0.75 kJ mol<sup>-1</sup>] result in greater deformation of the Co—S(1)—C(1) angle (114.1°, 4.60 kJ mol<sup>-1</sup>).

*trans*-N-[Co(L-met)<sub>2</sub>]<sup>+</sup> (2). The crystal-structure geometry is again well reproduced by the molecular-mechanics model and in this case the Co—S bonds are reproduced almost exactly. Disposition of the methyl group toward the less sterically demanding O donor atom is not possible in the *trans*-N isomer. The observed *S* configuration results in disposition toward the NH<sub>2</sub> group giving rise to unfavourable close contacts [HN(1A)⋯C(1'), 2.46 Å, 0.55 kJ mol<sup>-1</sup>] and opening of the Co—S—C(1) angle to 110.4° (2.95 kJ mol<sup>-1</sup>). The alternative *R* configuration results in a disposition toward the S donor atom. When only one ligand adopts the *R* configuration the strain energy calculated is slightly lower but when both adopt *R* configurations the strain energy increases by 8–9 kJ mol<sup>-1</sup> because the methyl groups are then disposed toward one another resulting in further deformation of the Co—S—C(1) angle (113.6°, 4.37 kJ mol<sup>-1</sup>). The strain energies indicate that roughly equal proportions of the *S,S* and *R,S* configurations would be expected but none of the *R,R* configuration. The <sup>1</sup>H NMR

spectrum of the *trans*-N isomer showed three peaks indicating a mixture of *R,S* and probably *S,S* configurations (Hidaka *et al.*, 1974).

*trans*-O-[Co(L-met)<sub>2</sub>]<sup>+</sup> (3). The crystal structure of the *trans*-O isomer revealed one conformationally disordered ligand, the six-membered ring in that case alternating between chair and boat conformations. Strain energies were calculated for both conformers. Comparison of crystal structure and energy-minimized geometries again shows good agreement with the Co-S bond lengths well reproduced. In the *trans*-O isomer the *R,S* configuration results in disposition of the methyl groups toward O and S donor atoms respectively. In the chair conformer the methyl group is disposed less directly toward the ligating O atom and more into the face of the ligand than in the boat conformer.

For the boat conformer the *R,R* configuration is favoured slightly (2 kJ mol<sup>-1</sup>) over the *R,S*, but the *S,S* is much less stable as a result of disposition of the methyl groups toward one another. The *R,R* and *S,S* configurations are of similar stability in the case of the chair conformer. The chair conformer is more than 7 kJ mol<sup>-1</sup> more stable than the boat suggesting that the appearance of the latter may be the result of crystal-packing and hydrogen-bonding effects. The comparable stability of all configurations for the chair conformer suggests that the three should be present in solution and this was the interpretation given of the <sup>1</sup>H NMR spectrum of the *trans*-O isomer (Hidaka *et al.*, 1974).

*trans*-S-[Co{(S)-Me-L-cys}<sub>2</sub>]<sup>+</sup>. Only one isomer and conformer of the (S)-Me-L-cys complex was considered, for comparison with the previously reported crystal structure. The crystal structure is reproduced well with the calculated Co-S bond length less than one standard deviation from the solid-state value (De Meester & Hodgson, 1976). It is interesting that the Co-S distance is so well reproduced for the *trans*-S-[Co{(S)-Me-L-cys}]<sup>+</sup> complex and suggests that the long bond in the crystal structure of the *trans*-S-[Co(L-met)<sub>2</sub>]<sup>+</sup> complex may be the result of solid-state effects rather than electronic *trans* effects.

There is considerably less deformation of the Co-S-C angles in the (S)-Me-L-cys complex and this is also reproduced in the molecular-mechanics model. The change to a five-membered chelate ring from a six-membered ring reduces the strain on the Co-S(1)-C(2) angle. The difference in the conformation of this ring results in the disposition of the methyl group over the middle of the O-Co-O angle rather than over one of the O atoms, resulting in fewer unfavourable interactions between the methyl groups and the ligating atoms and so less strain on the Co-S(1)-C(1) angle.

#### Concluding remarks

The crystal-structure analyses confirm the assignments of the *F*<sub>1</sub>, *F*<sub>2</sub> and *F*<sub>3</sub> bands from the preparation of

Hidaka *et al.* (1974) as the *trans*-S, *trans*-N and *trans*-O geometric isomers respectively. Their assignments of the configurational isomers are also consistent with those found in the crystal structures. The Co-S bond lengths are significantly longer in the *trans*-S isomer than the other two isomers suggesting that the S(sulfide) atom exerts a weak *trans* effect.

The molecular-mechanics model gives strain-energy differences which are consistent with the geometric and configurational isomer preferences of [Co(L-met)<sub>2</sub>]<sup>+</sup> determined from solution studies and reproduces well the structures of all isomers and of *trans*-S-[Co{(S)-Me-L-cys}<sub>2</sub>]<sup>+</sup>. In the case of structure (3), a conformer calculated to be of high energy was observed. However, in these structures there are numerous strong hydrogen bonds which might promote an otherwise unfavourable geometry. Since the conformer preferences obtained in solution, where hydrogen bonding is less likely to promote unfavourable conformers, are reproduced it appears that the model is valid for interactions of Co<sup>III</sup> with sulfide-sulfur-containing amino acids.

The strain energies of the most stable configuration for each isomer are very similar (100.5, 98.1 and 99.5 kJ mol<sup>-1</sup>) indicating that a nearly equal mixture of the three would be expected from an equilibrated preparation as is, indeed, observed experimentally (Hidaka *et al.*, 1974).

The configuration adopted by the S(Me) group is dictated by the favourability of the subsequent disposition of the methyl group with respect to interligand interactions. For the *trans*-S and *trans*-N isomers the *S* configuration is most favourable and for the *trans*-O isomer the *R* configuration is preferred.

The conformational isomerism is dominated by intraligand interactions. The chair conformation of the six-membered ring is preferred to the boat. Co-S bond lengths are significantly influenced by steric interactions; however, a weak *trans* effect cannot be ruled out for the S(sulfide) atom.

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## The Influence of Intermolecular Interactions on the Electron-Density Distribution. A Comparison of Experimental and Theoretical Results for $\alpha$ -Oxalic Acid Dihydrate\*

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### Abstract

The experimental electron-density distribution in  $\alpha$ -oxalic acid dihydrate,  $\alpha$ -C<sub>2</sub>H<sub>2</sub>O<sub>4</sub>·2H<sub>2</sub>O, as measured by Dam, Harkema & Feil [*Acta Cryst.* (1983), **B39**, 760–768], is compared with results from a theoretical density-functional calculation, with a local approximation to exchange and correlation. The agreement between the multipole-refined experimental and the refined vibrationally averaged theoretical electron-density distribution improves significantly when taking into account the effects of hydrogen bonding and crystal environment. A comparison of structure factors based on the experimental electron-density distribution with those based on the vibrationally averaged theoretical molecular-density distributions, yielded an *R* factor of 1.3%. Inclusion of the effects of hydrogen bonding in the theoretical model lowered the *R* factor to 1.1%. When the effects of the crystal environment were taken into account, a further lowering to 1.0% resulted.

### Introduction

As part of a recent project of the International Union of Crystallography, the electron-density distribution in  $\alpha$ -oxalic acid dihydrate has been thoroughly investigated, using both experimental and theoretical

techniques (Coppens *et al.*, 1984). The largest discrepancies between experiment and theory appeared to occur in the lone-pair regions where theoretical deformation densities (*i.e.* the difference between the molecular density and the superimposed spherically averaged densities of the free atoms constituting the molecule) are higher and less diffuse compared with the experimental deformation density. The cause of this discrepancy may well be ascribed to the limited basis set used and, as suggested by Olovsson (1980), Stevens (1980) and Hermansson (1984, 1985), the neglect of taking into account intermolecular interactions in the theoretical calculations.

The main object of this study is a comparison of the electron-density distribution in  $\alpha$ -oxalic acid dihydrate obtained from X-ray diffraction experiments on single crystals with those obtained from quantum-mechanical calculations. Therefore, the subject of a theoretical calculation should also be a system consisting of a large cluster of properly oriented and positioned interacting molecules. Since this approach is not feasible from a computational point of view, the model has to be simplified considerably.

Previous studies (Krijn & Feil, 1986, 1987) indicated that the electron-density redistribution, upon forming weak hydrogen bonds, is dominated by a polarization contribution. Consequently, the effects of weak hydrogen bonds on the electron-density distribution can be accounted for by placing the molecule in the electric field of its weakly bonded neighbours. In the case of strong hydrogen bonds, however, the subtle interplay of exchange repulsion, charge transfer and polarization

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