the Cl(B)–Ir–Cl(B)' and Cl(B)–Rh–Cl(B)' angles being acute, with values of 79.55 (12) and 81.71 (3)°, respectively.

A final point of possible relevance is the observation that the M···M distances in the $[(\eta^5\text{-}C_5Me_5)MCl]_2(\mu\text{-}Cl)_2$ species vary significantly, with values of 3.769 (1) Å for Ir···Ir and 3.719 (1) Å for Rh···Rh; in contrast to this, there is no significant difference between the Ir–Ir and Rh–Rh distances within the $[(\eta^5\text{-}C_5Me_5)MCl]_2(\mu\text{-}H)(\mu\text{-}Cl)$ species. This observation might be applicable as further evidence for direct metal–metal bonding in the μ-chloro-μ-hydrido species. However, further data are clearly required. We are currently attempting to synthesize μ-bromo-μ-hydrido and di-μ-bromo analogues in the expectation of clarifying these problems.

References and Notes

(1) M. R. Churchill and S. W. -Y. Ni, *J. Am. Chem. Soc.*, **95**, 2150 (1973).
(2) M. R. Churchill, S. A. Julis, and F. J. Rotella, *Inorg. Chem.*, **16**, 1137 (1977).
(3) C. White, D. S. Gill, J. W. Kang, H. B. Lee, and P. M. Maitlis, *J. Chem. Soc., Chem. Commun.*, 734 (1971); C. White, A. J. Oliver, and P. M. Maitlis, *J. Chem. Soc., Dalton Trans.*, 1901 (1973), and references contained therein.
(4) J. W. Kang, K. Moseley, and P. M. Maitlis, *J. Am. Chem. Soc.*, **91**, 5970 (1969).
(5) M. R. Churchill, R. A. Lashewycz, and F. J. Rotella, *Inorg. Chem.*, **16**, 265 (1977).
(6) "Syntex XTL Operations Manual", 2nd ed, Syntex Analytical Instruments, Cupertino, Calif., 1976.
(7) "International Tables for X-Ray Crystallography", Vol. IV, Kynoch Press, Birmingham, England, 1974: (a) pp 99–101; (b) pp 149–150.
(8) Esd's on average values are calculated from the "scatter formula", viz.

$$\sigma(av) = \left[\sum_{i=1}^{i=N} (d_i - \bar{d})^2 / (N-1) \right]^{1/2}$$

Here $\bar{d}$ is the average of N equivalent measurement and d_i is the ith such measurement.
(9) R. D. Shannon and C. T. Prewitt, *Acta Crystallogr., Sect. B*, **25**, 925 (1969).
(10) R. D. Shannon, *Acta Crystallogr., Sect. A*, **32**, 751 (1976).
(11) C. H. Wei, G. R. Wilkes, and L. F. Dahl, *J. Am. Chem. Soc.*, **89**, 4792 (1967).
(12) V. Albano, P. Bellon, and V. Scatturin, *Chem. Commun.*, 730 (1967).
(13) M. R. Churchill and B. G. DeBoer, *Inorg. Chem.*, **16**, 878 (1977).
(14) $[H_2Re_3(CO)_{12}^-]$: M. R. Churchill, P. H. Bird, H. D. Kaesz, R. Bau, and B. Fontal, *J. Am. Chem. Soc.*, **90**, 7135 (1968).
(15) $[HRe_3(CO)_{12}^{2-}]$: S. W. Kirtley, H. D. Kaesz, M. R. Churchill, and C. Knobler, in preparation; see also H. D. Kaesz, *Chem. Br.*, **9**, 344 (1973).
(16) $[H_6Re_4(CO)_{12}^{2-}]$: H. D. Kaesz, B. Fontal, R. Bau, S. W. Kirtley, and M. R. Churchill, *J. Am. Chem. Soc.*, **91**, 1021 (1969).

Tridentate Coordination by the L-Cysteine Dianion. Crystal and Molecular Structure of Sodium Bis(L-cysteinato)chromate(III) Dihydrate

PATRICE de MEESTER,[1a] DEREK J. HODGSON,*[1a] HANS C. FREEMAN,*[1b] and CHRISTOPHER J. MOORE[1b]

The crystal and molecular structure of the title complex, $Na[Cr(L\text{-}cys)_2]\cdot2H_2O$, $C_6H_{14}CrN_2NaO_6S_2$, has been determined from x-ray three-dimensional data. The complex crystallizes in the space group $P3_121$ of the trigonal system with a cell of dimensions $a = 10.644$ (2) and $c = 9.809$ (3) Å. There are three formula units per cell. Full-matrix least-squares refinement using 1221 independent reflections has reached $R = 0.022$. The structure contains $[Cr(L\text{-}cys)_2]^-$ anions, sodium cations, and two water molecules of solvation. The Cr and Na atoms as well as the oxygen atoms of the water molecules lie in special positions on diad axes. The complex anion has its central Cr atom in a slightly distorted octahedral coordination with two Cr–S, two Cr–O, and two Cr–N bonds respectively at distances 2.416 (1), 1.981 (1), and 2.062 (2) Å. Cis angles at the Cr atom range from 82.83 (6) to 94.33 (5)°. The two carboxylate oxygens and the two amino nitrogen atoms are mutually cis, while the two sulfur atoms are trans. The sodium cation has a more severely distorted octahedral geometry with its six coordination sites occupied by two pairs of water molecules and two Cr-bonded carboxylate oxygen atoms of one complex. The Na–O distances lie between 2.363 (2) and 2.473 (2) Å, and the cis bond angles range from 80.01 (8) to 102.01 (7)°. The structure contains hydrogen bonds of the type N–H···O, W–H···S, and W–H···O, where W is a water oxygen atom.

Introduction

The interactions of sulfur-containing amino acids and their derivatives with transition metal ions have been a subject of great interest in recent years because of the potential use of these ligands in metal chelation therapy.[2a] Among cysteine derivatives, penicillamine (β,β'-dimethylcysteine) and N-acetylpenicillamine are clinically used for the treatment of metal poisoning.[2b-5] Nevertheless, in this field, the knowledge of the nature and the extent of the metal bonding to cysteine and its derivatives is of primary importance and this is best obtained from x-ray structural studies. Up to now, only a limited number of such crystallographic determinations is available. These include several mercury complexes of pen (penicillamine)[6-8] and cys (cysteine),[9] lead[10] and cadmium complexes of D-pen,[11] $Cu^I_8Cu^{II}_6(D\text{-}pen)_{12}Cl$,[12] $Pd(SMC)Cl_2$ (SMC is S-methylcysteine),[13] $Co^{III}(SMC)_2{}^+$,[14] $Co^{III}(L\text{-}his)\text{-}(D\text{-}pen)$,[15,16] $[Co_2^{III}(L\text{-}his)(D\text{-}pen)(D\text{-}his)(L\text{-}pen)]$,[15] $Cr^{III}(L\text{-}his)(D\text{-}pen)$,[15,16] $Co^{III}(D\text{-}pen)(L\text{-}pen)$,[17] and several complexes

of Mo^{18-21} with L-cys or its methyl or ethyl esters. Cysteine and its derivatives present three potential coordination sites for metal binding, these being S, N, and O. The structural studies have shown that in all cases the sulfur atom is coordinated to the metal and that one or two of the other sites are sometimes also involved. This contrasts with metal complexes of methionine, for which sulfur coordination to the metal ions has not been found in the complexes with Cd,[22] Zn,[23] and Cu,[24] although it does occur in complexes with Hg,[6] Pd,[25] and Pt.[26] Structural studies of metal complexes of cys and its derivatives also show that the metal–ligand bond distances vary widely. In some cases, one bond is much weaker than the others, but in other examples all bonds are apparently of approximately equal strength. To this last class belong the tridentate complexes formed between pen and Co(III) and Cr(III).

Crystal structure analyses of $Na[Cr(L\text{-}cys)_2]\cdot2H_2O$ have recently been carried out independently at Chapel Hill and

Table I. Fractional Coordinates with Esd's in Parentheses

Atom	x	y	z
Cr	0.410 14 (4)	0	$-^1/_6$
S	0.517 37 (6)	0.193 16 (5)	-0.000 54 (4)
N	0.473 5 (2)	-0.104 4 (2)	-0.029 3 (2)
O(1)	0.233 8 (1)	-0.099 2 (2)	-0.051 8 (1)
O(2)	0.172 0 (2)	-0.155 7 (2)	0.166 4 (2)
C(1)	0.260 5 (2)	-0.117 8 (2)	0.072 7 (2)
C(2)	0.414 7 (3)	-0.083 3 (2)	0.100 4 (2)
C(3)	0.506 1 (3)	0.075 5 (3)	0.140 4 (2)
Na	0.095 3 (1)	0	$-^1/_6$
W(1)	-0.203 3 (3)	0	$^1/_3$
W(2)	0.089 8 (3)	0	$^1/_3$
H(1)	0.459 (4)	0.093 (4)	0.214 (3)
H(2)	0.587 (4)	0.090 (4)	0.160 (3)
H(3)	0.403 (3)	-0.147 (3)	0.168 (2)
H(4)	0.437 (3)	-0.182 (3)	-0.043 (3)
H(5)	0.564 (4)	-0.069 (4)	-0.024 (3)
H(6)	-0.217 (4)	0.074 (4)	0.343 (4)
H(7)	0.095 (6)	-0.053 (5)	0.284 (3)

Sydney. The existence of the parallel investigations was discovered only when the work had been completed.[27] There were no significant differences between the two sets of results. We here report the preparation and structure of the complex. The numerical values are taken from the Chapel Hill structure analysis in view of their slightly higher precision.

Experimental Section

Crystals of the complex were prepared in the following manner. Chromium nitrate monohydrate (2.5×10^{-3} mol) in 15 mL of water was mixed with 7.5×10^{-3} mol of L-cysteine in 15 mL of water. The resulting solution was boiled for a few minutes and solid NaOH was added until the solution's color changed from red-violet to blue; at this stage the pH was approximately 7. The hot solution was then filtered and allowed to stand. After one night, large well-formed crystals appeared; in one of our preparations one single crystal which formed was found to weigh as much as 26 mg. The crystals look almost black, but when they are ground, the powder is blue. The potassium analogue was also obtained as single crystals, by using KOH in place of the NaOH.

Preliminary Weissenberg and precession photographs showed that the crystals of the complex were trigonal, the space group being either $P3_1$, $P3_112$, or $P3_121$ (or their enantiomorphs) with $000l$, $l = 3n + 1$, as their only systematic absences. Inspection of the films showed that the equivalencies between observed intensities were consistent only with the space groups $P3_121$ and $P3_221$. The cell constants were obtained by least-squares methods. The potassium analogue of the title complex is strictly isomorphous.

Crystal data: $C_6H_{14}O_6N_2S_2NaCr$, mol wt 349.3, trigonal, space group $P3_121$ (No. 152), $Z = 3$, μ(Mo Kα) = 12.97 cm^{-1}. de Meester and Hodgson: a = 10.644 (2), c = 9.809 (3) Å; V = 962.4 Å^3; d_{measd} = 1.79 (3), d_{calcd} = 1.808 g cm^{-3}. Freeman and Moore: a = 10.653 (1), c = 9.797 (2) Å; V = 962.8 Å^3; d_{measd} = 1.78 (3), d_{calcd} = 1.802 g cm^{-3}.

Data Collection—Chapel Hill. A crystal of approximate dimensions $0.31 \times 0.44 \times 0.59$ mm was mounted on a Picker four-circle automatic diffractometer with its c axis roughly parallel to the machine ϕ axis.

Data were collected out to 2θ(Mo) = 65° in a manner described elsewhere.[14] The data were processed by the procedure of Ibers and co-workers.[28,29] The intensities were corrected for Lorentz and polarization effects and for absorption, the transmission coefficients ranging from 0.67 to 0.76.[30] Of the data gathered, 1221 independent intensities had $I > 2.6\sigma(I)$.

Data Collection—Sydney. The data were recorded on a computer-controlled Supper equiinclination diffractometer,[31] using a crystal mounted with its axis of rotation parallel to the crystallographic b axis. A total of 3992 reflections were measured on the layers $h0l$–$h7l$ ($2\theta < 60°$, monochromated Mo Kα radiation). Lorentz, double-polarization, and absorption corrections were applied. The diamond-shaped crystal specimen had well-developed faces of the forms {101}, {011}, and {11$\bar{1}$} with equal perpendicular interfacial distances of 0.26 mm. The transmission coefficients were in the range 0.77–0.83. Equivalent reflections on different layers were used to bring the intensities to a common scale.[32] After averaging, there were 1066 independent reflections, of which 895 had $I > 2.9\sigma(I)$. The standard deviations of the structure factors were calculated with allowance for random and systematic errors.[33]

Solution and Refinement of the Structure. In the Chapel Hill structure analysis, the locations of the chromium and sulfur atoms were derived from a three-dimensional Patterson function, and these positions were refined by least-squares methods. All least-squares calculations were on F, the function minimized being $\sum w(F_o - F_c)^2$. The weights w were taken as $4F_o^2/\sigma^2(F_o)^2$. Form factors for nonhydrogen atoms were taken from ref 34 while those for H were from Stewart, Davidson, and Simpson.[35] The effects of the anomalous dispersion of Cr and S were included in F_c,[36] the values of $\Delta f'$ and $\Delta f''$ being taken from ref 34.

A difference Fourier map calculated on the basis of the positions of the Cr and S atoms alone showed the positions of the remaining nonhydrogen atoms in space group $P3_221$. Isotropic refinement reduced R_1 to 0.090 and R_2 to 0.137, with R_1 defined as $\sum||F_o| - |F_c||/\sum|F_o|$ and R_2 as $[\sum w(|F_o| - |F_c|)^2/\sum w(F_o)^2]^{1/2}$. At this stage it was apparent that we had chosen the wrong enantiomer, since our model contained the D isomer of the ligand. Refinement in the enantiomorphous space group $P3_121$ yielded R_1 = 0.083 and R_2 = 0.132. All hydrogen atoms were found in a difference Fourier map after anisotropic refinement of the nonhydrogen atoms. Inspection of the observed and calculated structure amplitudes near the end of the refinement indicated that there were significant errors in the data due to secondary extinction. A correction of the type described by Zachariasen[37] was, therefore, applied. The refined value of the extinction coefficient was 3.9 (1) $\times 10^{-7}$. No parameter shift in the final least-squares cycle was greater than 0.2σ. A final difference Fourier revealed no significant electron density, with no peak higher than 0.37 e Å^{-3}. The value of R_2 showed no significant dependence on $\sin \theta$ or on $|F_c|$. The final agreement factors R_1 and R_2 are 0.022 and 0.030, respectively. The positional and thermal parameters for all atoms are presented in Tables I and II. A compilation of observed and calculated structure factors is available.[39]

The Sydney structure analysis proceeded along essentially identical lines, except that no correction for extinction was made, and refinement weights w were taken as $\sigma^{-2}(F_o)$ [where the standard deviations $\sigma(F_o)$ were derived as mentioned previously]. The final residuals R_1 and R_2 were 0.036 and 0.036, respectively.

There are no differences greater than 2 esd's between equivalent positional parameters of nonhydrogen atoms derived from the two

Table II. Thermal Parameters with Esd's in Parentheses

Atom	$\beta_{11}{}^a$	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}	Atom	B, Å^2
Cr	0.004 33 (3)	0.004 77 (4)	0.003 37 (3)	$[0.002\ 39]^b$	-0.000 02 (1)	[-0.000 04]	H(1)	4.4 (7)
S	0.007 28 (6)	0.005 04 (5)	0.004 86 (4)	0.002 51 (4)	-0.000 52 (4)	-0.000 63 (3)	H(2)	4.6 (8)
N	0.007 4 (2)	0.007 4 (2)	0.005 6 (1)	0.005 2 (2)	-0.000 3 (1)	-0.000 2 (1)	H(3)	2.8 (6)
O(1)	0.005 4 (1)	0.006 7 (2)	0.005 0 (1)	0.002 9 (1)	0.000 4 (1)	0.001 0 (1)	H(4)	2.1 (5)
O(2)	0.012 8 (2)	0.012 3 (2)	0.007 4 (2)	0.007 5 (2)	0.005 3 (2)	0.003 8 (2)	H(5)	3.0 (6)
C(1)	0.008 0 (2)	0.005 4 (2)	0.005 1 (1)	0.003 6 (2)	0.001 4 (1)	0.001 2 (1)	H(6)	4.2 (8)
C(2)	0.008 8 (2)	0.006 7 (2)	0.004 1 (1)	0.004 6 (2)	-0.000 6 (1)	0.000 4 (1)	H(7)	7.2 (14)
C(3)	0.010 4 (3)	0.007 3 (2)	0.005 0 (2)	0.003 5 (2)	-0.002 1 (2)	-0.000 8 (2)		
Na	0.007 3 (1)	0.008 8 (2)	0.006 4 (1)	[0.004 4]	-0.000 1 (1)	[-0.000 2]		
W(1)	0.008 5 (2)	0.008 4 (3)	0.011 2 (3)	[0.004 2]	0.001 0 (1)	[0.002 0]		
W(2)	0.008 4 (2)	0.011 1 (3)	0.008 7 (3)	[0.005 6]	-0.000 1 (1)	[-0.000 2]		

^{a} The form of the anisotropic thermal ellipsoid is $\exp[-(\beta_{11}h^2 + \beta_{22}k^2 + \beta_{33}l^2 + 2\beta_{12}hk + 2\beta_{13}hl + 2\beta_{23}kl)]$. ^{b} Brackets indicate that for atoms in special positions on diad axes $\beta_{22} = 2\beta_{12}$ and $\beta_{23} = 2\beta_{13}$.

Table III. Bond Distances (Å) and Bond Angles (deg)

Cr–S	2.416 (1)	C(2)–N	1.484 (3)
Cr–N	2.062 (2)	C(2)–C(1)	1.518 (3)
Cr–O(1)	1.981 (1)	C(1)–O(1)	1.291 (2)
S–C(3)	1.829 (2)	C(1)–O(2)	1.231 (2)
C(3)–C(2)	1.521 (3)		

S–Cr–S^{I} ^{a}	174.6 (1)	Cr–S–C(3)	94.92 (7)
S–Cr–O(1)	89.33 (5)	Cr–N–C(2)	101.7 (1)
S–Cr–N	82.83 (6)	Cr–O(1)–C(1)	113.4 (1)
S–Cr–N^I	93.95 (6)	C(3)–C(2)–N	107.8 (2)
S–Cr–O(1)^I	94.33 (5)	C(3)–C(2)–C(1)	109.1 (2)
N–Cr–O(1)	79.59 (6)	N–C(2)–C(1)	107.2 (1)
O(1)–Cr–O(1)^I	94.15 (8)	C(2)–C(1)–O(2)	120.2 (2)
N–Cr–N^I	106.8 (1)	C(2)–C(1)–O(1)	115.3 (2)
O(1)–Cr–N^I	173.13 (9)	O(1)–C(1)–O(2)	124.5 (2)

Na$\cdots$W(1)^{II}	2.488 (2)	Na$\cdots$O(1)	2.472 (2)
Na$\cdots$W(2)^{II}	2.363 (2)		

W(2)^{II}–Na–W(2)^{III}	101.68 (6)	O(1)–Na–O(1)^I	71.87 (7)
W(2)^{II}–Na–O(1)	162.96 (5)	O(1)–Na–W(1)^{II}	89.95 (7)
W(2)^{II}–Na–O(1)^I	93.81 (3)	O(1)–Na–W(1)^{III}	87.53 (4)
W(2)^{II}–Na–W(1)^{II}	80.00 (8)	W(1)^{II}–Na–W(1)^{III}	176.89 (9)
W(2)^{II}–Na–W(1)^{III}	101.99 (6)		

Hydrogen Bonding

A–B$\cdots$C	A$\cdots$C	B$\cdots$C	A–B–C
N–H(5)$\cdots$O(2)^{IV}	2.888 (3)	2.40 (3)	118 (3)
W(1)–H(6)$\cdots$S^V	3.389 (2)	2.55 (3)	156 (3)
W(2)–H(7)$\cdots$O(2)	2.764 (3)	2.02 (4)	163 (5)

^{a} Roman superscripts refer to atoms in the following positions: (I) $x - y, -y, -^1/_3 - z$; (II) $y, x, -z$; (III) $-x, y - x, ^1/_3 - z$; (IV) $1 + y - x, -x, z - ^1/_3$; (V) $-y, x - y, ^1/_3 + z$.

Table IV. Dihedral Angles of Interest (deg)

O(1)–C(1)–C(2)$^\alpha$–C(3)	90.0^a	Cr–N–C(2)$^\alpha$–C(1)	45.7
O(1)–C(1)–C(2)$^\alpha$–N	−26.4	Cr–O(1)–C(1)–C(2)$^\alpha$	−9.4
S–C(3)–C(2)$^\alpha$–N	52.5	Cr–S–C(3)–C(2)$^\alpha$	−10.2
Cr–N–C(2)$^\alpha$–C(3)	−71.7		

^{a} Values are taken as positive when far atom rotates anticlockwise relative to near atom to be eclipsed.

analyses. A half-normal probability plot[38] shows that there are no systematic differences between the two sets of positional and thermal parameters but that the standard deviations of the parameter *differences* have been underestimated by about 40%. Tables I and II show the positional and thermal parameters for all atoms from the Chapel Hill calculations. The Sydney parameters and lists of observed and calculated structure factors from both analyses are available.[39] The principal bond lengths and angles are listed in Tables III and IV.

Discussion

The structure contains the complex anion [Cr(L-cys)$_2$]$^-$, Na$^+$ cations, and water molecules of solvation. The geometry of the complex anion is shown in Figure 1. The central Cr(III) atom lies on a twofold axis and its coordination is approximately octahedral, the two cysteine ligands being tridentate via trans S atoms and cis O and N atoms. The Cr–O bond of length 1.981 (1) Å is relatively strong and can be compared to distances found in a variety of complexes, typically in tris(glycinato)chromium(III)[40] where they average 1.965 (2) Å and in tris(1,3-propanedionato)chromium(III)[41] where the average is 1.954 (4) Å. The Cr–N bond of 2.062 (2) Å is also strong. In [Cr(NH$_2$(CH$_2$)$_3$NH$_2$)$_3$][42] the Cr–N bonds average 2.096 (3) Å, and in [Cr(gly)$_3$][40] the mean value is 2.068 (5) Å. The Cr–S distance found in the title complex is 2.416 (1) Å. Values previously reported for this distance in similar complexes are 2.400 (1) Å (average of 12 bonds) in tris(ethyl thioxanthato)chromium(III),[43] 2.389 (5) Å in [Cr(mercaptoethylamine)$_2$(en)],[44] 2.332 (2) Å in [Cr(L-his)(D-pen)],[15,16] and 2.337 (2) Å in [Cr(mercaptoacetato)(en)$_2$].[45] The longer
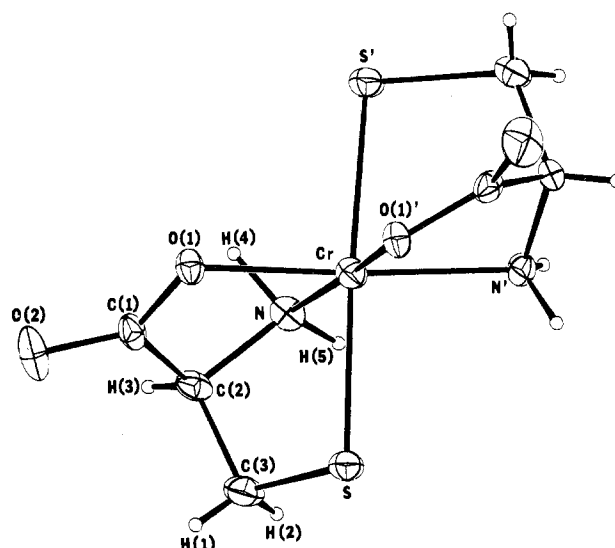
Figure 1. View of the [Cr(L-cys)$_2$]$^-$ anion in Na[Cr(L-cys)$_2$]·2H$_2$O. Thermal ellipsoids are drawn at the 40% probability level, with hydrogen atoms shown as spheres of arbitrary size.
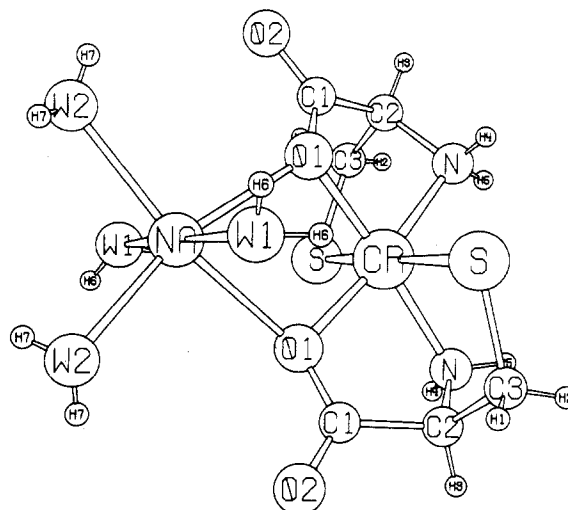

Figure 2. Perspective view of sodium ion in relation to the [Cr(L-cys)$_2$]$^-$ anion in Na[Cr(L-cys)$_2$]·2H$_2$O. Three diad axes run respectively through the Na and Cr atoms, the water molecules W(1) and W(2) close to the reader, and the water molecules W(1) and W(2) remote from the reader.

Cr–S bonds are found in complexes where they are trans to other S donor atoms. The cis angles at the Cr atom are normal, ranging from 82.83 (6) to 94.33 (5)°, and are very similar to those found in related complexes.[14–17]

The bond distances obtained for the L-cysteine ligand in this study are precise, with estimated standard deviations of 0.002–0.003 Å. The values are compared to those found for the orthorhombic form of L-cysteine[46] and in some related metal complexes in Table V. Equivalent bonds have similar lengths in all of the structures. The only exceptions are the C–O bonds, where the difference between bound and unbound carboxy oxygen atoms in the metal complexes is not found in the free ligand.

The sodium cation is in an approximately octahedral environment, being surrounded by two pairs of water molecules and the two Cr-bonded carboxy oxygen atoms of one complex (Figure 2). The cis angles range from 80.00 (8) to 101.68 (6)°, and the Na–O distances, from 2.363 (2) to 2.488 (2) Å. This geometry is not very distorted and compares well with recent accurate determinations, e.g., in sodium urate[47] where the Na–O distances range from 2.351 (9) to 2.535 (9) Å and

Table V. Comparison of the Cysteine or Penicillamine Bond Lengths in Several Structures

Bond	$Cr(cys)_2^-$ (this work)	Cys^{46}	$Co(L\text{-his})(D\text{-pen})^{15,16}$	$Cr(L\text{-his})(D\text{-pen})^{15,16}$	$Co(D\text{-pen})(L\text{-pen})^{17}$
$S^\gamma-C^\beta$	1.829 (2)	1.811 (3)	1.838 (5)	1.845 (6)	1.848 (5)
$C^\beta-C^\alpha$	1.521 (3)	1.537 (3)	1.552 (9)	1.536 (8)	1.544 (5)
$C^\alpha-N$	1.484 (3)	1.493 (3)	1.482 (6)	1.511 (7)	1.482 (4)
$C^\alpha-C$	1.518 (3)	1.522 (3)	1.526 (3)	1.513 (7)	1.535 (5)
C-O	1.231 (2)	1.238 (3)	1.222 (5)	1.248 (6)	1.225 (4)
C-O	1.291 (2)^a	1.256 (3)	1.285 (5)^a	1.265 (6)^a	1.283 (4)^a

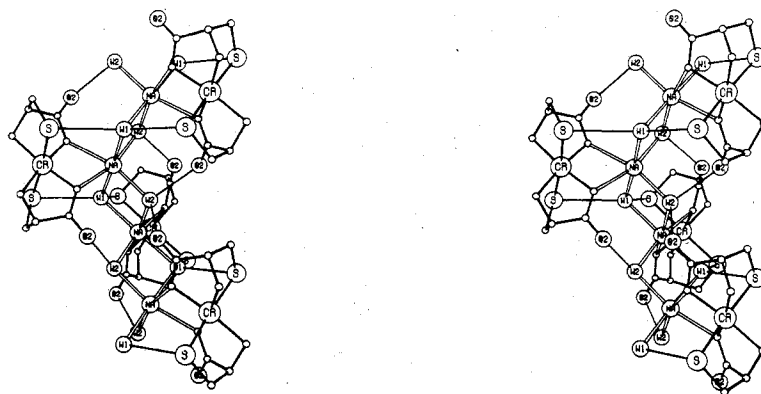^{a} Oxygen atom which is bonded to the metal.

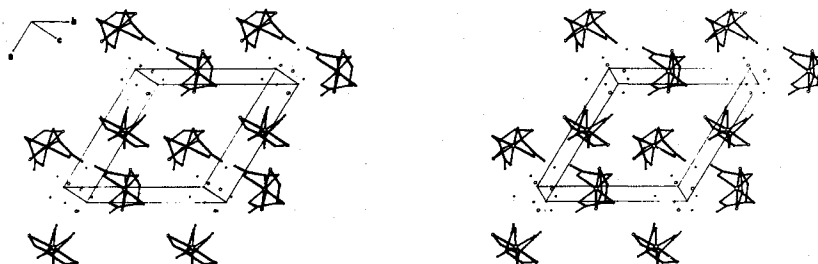**Figure 3.** Stereoscopic drawing of the structure viewed in a direction perpendicular to the 3_1 axis.

Figure 4. Stereoscopic drawing showing the packing of the complexes in the crystals of $Na[Cr(L\text{-cys})_2]\cdot 2H_2O$. The view is approximately along the crystallographic c axis.

the cis angles range from 75.8 (3) to 101.1 (3)° and also in the sodium salt of 5'-dAMP[48] with analogous values of 2.370 (6)–2.453 (6) Å and 87.2 (2)–93.1 (2)°. Thus the geometry around the sodium cation in the title complex represents, to a good approximation, the normal geometry of this ion. There are many known examples where the geometry around sodium is much more irregular.

The Na and Cr atoms lie on a diad axis, and the pairs of water molecules W(1) and W(2) lie on two other diads. The $(H_2O)_4Na(L\text{-cys})_2Cr$ motif is repeated by the threefold screw axis to form an infinite spiral (Figure 3). Adjacent Na ions in the spiral share a pair of W(1) and W(2) water molecules. There are also strong hydrogen-bonded interactions within the spiral, but interactions between neighboring spirals are weak (see below). The packing of the spirals results in the unusual trigonal symmetry of the crystals (Figure 4). The Na ions and water molecules are relatively close to the threefold axes while the complex anions are approximately midway between them.

There are several hydrogen bonds in this structure. The amino group of one complex anion forms such a bond with the terminal oxygen atom O(2) of a complex anion in a neighboring spiral. This interaction is weak, with N···O = 2.888 (3) Å, H···O = 2.40 (3) Å, and N-H···O = 118 (3)°. The other two types of hydrogen bonds are formed between atoms in the same spiral. There is a W(2)···O(2) interaction with a separation of 2.764 (3) Å and an associated angle of 163 (5)°. There is also a hydrogen bond of the type W-H···S

with a distance of 3.389 (2) Å and an angle at hydrogen of 156 (3)°. These values can be compared to those reported in 6-thioguanine picrate monohydrate[49] of 3.345 Å and 175°.

References and Notes

(1) (a) University of North Carolina. (b) University of Sydney.
(2) (a) J. J. Chisholm, *J. Pediatr.*, **73**, 1(1968); (b) H. V. Aposhian, *Science*, **128**, 93 (1958).
(3) J. M. Walshe, *Am. J. Med.*, **21**, 487 (1956).
(4) H. V. Aposhian and M. M. Aposhian, *J. Pharmacol. Exp. Ther.*, **126**, 131 (1959).
(5) R. A. P. Kark, D. C. Poskanzer, and J. Bullock, *N. Engl. J. Med.*, **285**, 10 (1971).
(6) A. J. Carty and N. J. Taylor, *J. Chem. Soc., Chem. Commun.*, 214 (1976).
(7) Y. S. Wong, P. C. Chieh, and A. J. Carty, *J. Chem. Soc., Chem. Commun.*, 741 (1973).
(8) Y. S. Wong, P. C. Chieh, and A. J. Carty, *Can. J. Chem.*, **51**, 2597 (1973).
(9) N. J. Taylor, Y. S. Wong, P. C. Chieh, and A. J. Carty, *J. Chem. Soc., Dalton Trans.*, 438 (1975).
(10) H. C. Freeman, G. N. Stevens, and I. F. Taylor, *J. Chem. Soc., Chem. Commun.*, 366 (1974).

(11) H. C. Freeman, F. Huq, and G. N. Stevens, *J. Chem. Soc., Chem. Commun.*, 90 (1976).

(12) P. J. Birker and H. C. Freeman, *J. Chem. Soc., Chem. Commun.*, 312 (1976).

(13) L. P. Battaglia, A. B. Corradi, C. G. Palmieri, M. Nardelli, and M. E. V. Tani, *Acta Crystallogr., Sect. B*, **29**, 762 (1973).

(14) P. de Meester and D. J. Hodgson, *J. Chem. Soc., Dalton Trans.*, 618 (1976).

(15) P. de Meester and D. J. Hodgson, *J. Chem. Soc., Chem. Commun.*, 280 (1976).

(16) P. de Meester and D. J. Hodgson, submitted for publication.

(17) H. M. Helis, P. de Meester, and D. J. Hodgson, submitted for publication.

(18) C. K. Prout, G. B. Allison, L. T. J. Delbaere, and E. Gore, *Acta Crystallogr., Sect. B*, **28**, 3043 (1972).

(19) J. R. Knox and C. K. Prout, *Acta Crystallogr., Sect. B*, **25**, 1857 (1969).

(20) M. G. B. Drew and A. Kay, *J. Chem. Soc. A*, 1846 (1971).

(21) M. G. B. Drew and A. Kay, *J. Chem. Soc. A*, 1852 (1971).

(22) R. J. Flook, H. C. Freeman, C. J. Moore, and M. L. Scudder, *J. Chem. Soc., Chem. Commun.*, 753 (1973).

(23) R. B. Wilson, P. de Meester, and D. J. Hodgson, to be submitted for publication.

(24) M. V. Veldis and G. J. Palenik, *Chem. Commun.*, 1277 (1969).

(25) R. C. Warren, J. F. McConnell, and N. C. Stephenson, *Acta Crystallogr., Sect. B*, **26**, 1402 (1970).

(26) H. C. Freeman and M. L. Golomb, *Chem. Commun.*, 1523 (1970).

(27) A preliminary account of the work at Chapel Hill has already been presented: D. J. Hodgson and P. de Meester, Centennial Meeting of the American Chemical Society, New York, N.Y., April 1976; see Abstracts, No. INOR 43.

(28) P. W. R. Corfield, R. J. Doedens, and J. A. Ibers, *Inorg. Chem.*, **6**, 197 (1967).

(29) W. R. Busing and H. A. Levy, *J. Chem. Phys.*, **26**, 563 (1957).

(30) For a description of the programs used, see E. D. Estes and D. J. Hodgson, *Inorg. Chem.*, **12**, 2932 (1973).

(31) H. C. Freeman, J. M. Guss, C. E. Nockolds, R. Page, and A. Webster, *Acta Crystallogr., Sect. A*, **26**, 149 (1970).

(32) (a) A. D. Rae, *Acta Crystallogr.*, **19**, 683 (1965); (b) A. D. Rae and A. B. Blake, *ibid.*, **20**, 586 (1966).

(33) H. C. Freeman and J. M. Guss, *Acta Crystallogr., Sect. B*, **28**, 2090 (1972).

(34) "International Tables for X-Ray Crystallography", Vol. IV, Kynoch Press, Birmingham, England, 1974.

(35) R. F. Stewart, E. R. Davidson, and W. T. Simpson, *J. Chem. Phys.*, **42**, 3175 (1965).

(36) J. A. Ibers and W. C. Hamilton, *Acta Crystallogr.*, **17**, 781 (1964).

(37) W. H. Zachariasen, *Acta Crystallogr., Sect. A*, 212 (1968).

(38) S. C. Abrahams and E. T. Keve, *Acta Crystallogr., Sect. A*, **27**, 157 (1971).

(39) Supplementary material.

(40) R. F. Bryan, P. T. Greene, P. T. Stokely, and E. W. Wilson, *Inorg. Chem.*, **10**, 1468 (1971).

(41) M. D. Glick, B. Andrelezyk, and R. L. Lintvedt, *Acta Crystallogr., Sect. B*, **31**, 916 (1975).

(42) F. A. Jurnak and K. N. Raymond, *Inorg. Chem.*, **13**, 2387 (1974).

(43) A. C. Villa, A. G. Manfredotti, C. Guastini, and M. Nardelli, *Acta Crystallogr., Sect. B*, **30**, 2788 (1974).

(44) C. Stein, S. Bouma, J. Carlson, C. Cornelius, J. Maeda, C. Weschler, E. Deutsch, and K. O. Hodgson, *Inorg. Chem.*, **15**, 1183 (1976).

(45) R. C. Elder, L. R. Florian, R. E. Lake, and A. M. Yacynych, *Inorg. Chem.*, **12**, 2690 (1973).

(46) K. A. Kerr and J. P. Ashmore, *Acta Crystallogr., Sect. B*, **29**, 2124 (1973).

(47) N. S. Mandel and G. S. Mandel, *J. Am. Chem. Soc.*, **98**, 2319 (1976).

(48) B. S. Reddy and M. A. Visuramitra, *Acta Crystallogr., Sect. B*, **31**, 19 (1975).

(49) C. E. Bugg and U. Thewalt, *Acta Crystallogr., Sect. B*, **31**, 121 (1975).

Contribution from the Department of Chemistry,
University of North Carolina, Chapel Hill, North Carolina 27514

Structural Characterization of Bis(L-methionato)zinc(II), Zn(L-met)₂

ROXY BREAM WILSON, PATRICE de MEESTER, and DEREK J. HODGSON*

AIC60754W

The crystal and molecular structure of bis(L-methionato)zinc(II), Zn(L-met)₂, has been determined from three-dimensional x-ray counter data. The complex crystallizes in the monoclinic space group $P2_1$ with two formula units in a cell with dimensions $a = 15.731$ (5) Å, $b = 5.119$ (2) Å, $c = 9.437$ (4) Å, and $\beta = 107.96$ (2)°. Least-squares refinement of the structure led to a value of the conventional R factor (on F) of 0.055 for 1083 data with $F^2 > 2\sigma(F^2)$. The complex consists of Zn(met)₂ units linked by long-range Zn–O contacts of 2.240 (7) and 2.729 (7) Å into sheets lying approximately in the crystallographic b–c plane. There is slightly distorted octahedral geometry around each zinc center, the base plane being occupied by the amino nitrogen atom and one carboxyl oxygen atom from each independent methionine moiety. The remaining carboxyl oxygen atoms participate in long-range Zn–O interactions. The geometry of the methionine ligands is similar to that of uncomplexed L-methionine. Polymeric interactions in Zn(L-met)₂ are similar to those found in Cu(DL-met)₂ and Cd(L-met)₂.

Introduction

Metal poisoning has become an unpleasant side effect of our technologically advanced society. Caused mainly by industrial pollution and the use of metals in household and agricultural products,[2] metal poisoning has been treated effectively with chelating agents.[3] Most commonly used in this capacity are ethylenediaminetetraacetic acid (EDTA),[4,5] 2,3-dimercaptopropanol (BAL, for British Anti-Lewisite),[6,7] and derivatives of cysteine such as β,β′-dimethylcysteine (penicillamine).[8–10] The nature and extent of the binding of cysteine and its derivatives with transition metals have been the topics of considerable research,[11–25] not only because of its importance in chelation therapy but also in catalysis.[11] Cysteine and penicillamine, which have been shown to occupy one, two, or three coordination sites depending on the metal, can form two five-membered and one six-membered chelate rings if they exhibit tridentate coordination. Tridentate methionine potentially forms one five-, one six-, and one seven-membered ring. However, no such metal complex of methionine has been isolated to date, and, in general, solid-state complexes of methionine are not as well characterized as those of cysteine and penicillamine. With Pt(II)[18] and Pd(II)[23] methionine acts as a bidentate chelate bonding through sulfur and nitrogen with the carboxyl group protonated. With the amino group but not the carboxyl group protonated, methionine coordinates to two different Hg(II) centers, one through sulfur and the other through both carboxyl oxygen atoms.[26] When neither the amino nor the carboxyl group is protonated and the metal is Cd(II)[27] or Cu(II),[22] methionine again interacts with two metal centers. It coordinates through the amino nitrogen and one carboxyl oxygen to one center and through the other carboxyl oxygen to the second metal center. As was the case for cysteine and penicillamine, the mode of methionine binding also varies depending on the metal atom.

Zinc is a much less toxic metal than other group 2B metals[28] and has been shown to compete successfully with cadmium for protein binding sites.[29] Thus, zinc complexes are most useful in comparison with their cadmium analogues. In order both to further examine the effect of increased chelate ring size on the extent of methionine binding to metals and to compare it with the cadmium analogue, we undertook the x-ray structural analysis of Zn(L-met)₂.

Experimental Section

The complex was prepared by adding an aqueous solution of L-methionine to a suspension of freshly prepared Zn(OH)₂ in water so that the molar ratio of ligand to metal was 2:1. The reaction mixture was filtered and the filtrate allowed to evaporate until colorless plates precipitated. Anal. Calcd for ZnS₂O₄N₂C₁₀H₂₀: Zn, 18.07; N, 7.74;