Metal–Penicillamine Interactions. Part 1. Preparation and Crystal Structure of a 1:1 Complex of Mercuric Chloride with D-Penicillamine, $2[(\mu_3\text{-Cl})\{HgSC(CH_3)_2CH(NH_3)COO\}_3]\cdot 3(\mu_2\text{-Cl})\cdot 2(H_3O)\cdot(H_2O\cdot Cl)_3$

LANGFORD BOOK

Department of Chemistry, Nankai University, Tianjin, China

and THOMAS C. W. MAK*

Department of Chemistry, The Chinese University of Hong Kong, Shatin, New Territories, Hong Kong

Received January 31, 1984

A 1:1 complex of mercuric chloride with D-penicillamine has been isolated and characterised as $2[(\mu_3\text{-Cl})\{HgSC(CH_3)_2CH(NH_3)COO\}_3]\cdot 3(\mu_2\text{-Cl})\cdot 2(H_3O)\cdot(H_2O\cdot Cl)_3$. *The compound crystallises in cubic space group* $P4_132$, *with* $a = 18.679(5)$ Å *and* $Z = 4$. *The structure, refined to* $R_F = 0.086$ *for 443 observed Mo-Kα diffractometer data, features a triply bridging chloride ion linking three equivalent* $[HgSC(CH_3)_2CH(NH_3)COO]^+$ *units* [Hg–Cl = 2.37(1) Å, Hg–Cl–Hg′ = 98.5(9)°]. *The carboxylate groups of a pair of adjacent penicillamine ligands are strongly linked* via *a symmetrical* O···H···O *hydrogen bond of length 2.24(8) Å, and neighboring pyramidal trinuclear* $[(\mu_3\text{-Cl})\{HgSC(CH_3)_2CH(NH_3)COO\}_3]^{2+}$ *moieties are further connected by symmetrical chloride bridges* [Hg–Cl = 3.06(2) Å; Hg–Cl–Hg″ = 79.6(7)°] *to form a three-dimensional network. The voids in the lattice are filled by hydronium ions and novel planar cyclic hydrogen-bonded* $(H_2O\cdot Cl^-)_3$ *rings of edge* O–H···Cl = 2.46(4) Å.

Introduction

The chemical behaviour of the element mercury differs significantly from those of its congeners zinc and cadmium, particularly as it relates to biochemistry and toxicology. In contrast to zinc, which is an important biological metal, mercury acts as a protein inhibitor in biological systems. Mercuric chloride, one of the important inorganic mercury pollutants, is a largely covalent molecule which remains undissociated in aqueous solution. Its interaction with sulfhydryl amino acids is in most cases the key to the biochemical action of inorganic mercury. While L-cysteine is usually used as a model for the behaviour of cysteinyl-containing proteins towards mercurials, D-penicillamine and its derivatives constitute one of the most effective classes of antidotes for mercury poisoning. X-Ray structural studies have demonstrated linear or tetrahedral coordination of sulfhydryl groups or chloride ions around Hg^{2+} ions in the 1:2 and 1:1 $HgCl_2$/L-cysteine complexes [1], linear S–Hg–S coordination in the 1:2 $HgCl_2$/D,L-penicillamine complex, and diagonal Cl–Hg–S coordination in the 2:1 $HgCl_2$/D,L-penicillamine complex [2]. In the last complex, $(HgCl_2)_2[SC(CH_3)_2CH(NH_3)COOH]\cdot 2H_2O$, the $[Cl–Hg–SC(CH_3)_2CH(NH_3)COOH]^+$ and $[HgCl_3]^-$ structural units are interlinked by a weak thioether-type bridge from the penicillamine ligand. In solution, the complex readily dissociates into $[Cl–Hg–S]^+$ and $[HgCl_3]^-$ ions [3]. Since the existence of a $[ClHgSC(CH_3)_2CH(NH_3)COOH]^+$ cation, and of similar species with different sulfhydryl amino acids like homocysteine and cysteine, has been postulated in one possible mechanism for environmental methylmercury formation [4, 5], it is desirable to isolate this 1:1 $HgCl_2$/penicillamine complex for structural analysis. In the present work, we report the synthesis and structural characterisation of a complex of stoichiometry $C_{30}H_{72}Cl_8Hg_6N_6O_{17}S_6$, of which a preliminary study has appeared as part of a doctoral dissertation [6].

Experimental

Preparation

Mercuric chloride (7 mmol in 20 ml ethanol) was added to D-penicillamine free base (7 mmol in 20 ml water) with stirring for 10 minutes. The resulting solution was then allowed to evaporate slowly at room temperature. Colourless rhomboidal dodecahedral crystals were obtained. Similar prepara-

*Author to whom correspondence should be addressed.

0020-1693/84/$3.00

© Elsevier Sequoia/Printed in Switzerland

TABLE I. Data Collection and Processing Parameters.

Molecular formula	$C_{30}H_{72}Cl_8Hg_6N_6O_{17}S_6$
Formula weight	2468.49
Cell constants	a = 18.679(5) A, V = 6518(6) A^3
Density	D_c = 2.516 (Z = 4), D_m = 2.60 g cm^{-3}
Space group	$P4_132$
Crystal size	average radius R = 0.04 cm
Radiation	graphite monochromatized Mo-K_α (λ = 0.71069 A)
μ(Mo-K_α)	146.67 cm^{-1}
Mean μR	2.7
Transmission factors	0.004–0.013
Scan type and speed	θ–2θ; 2.55 to 14.55 deg min^{-1}
Scan range (2θ)	0.7° below $K_{\alpha1}$ to 0.7° above $K_{\alpha2}$
Collection range	h, k, l ($h \leqslant k \leqslant l$); $2\theta < 45°$
Background counting	stationary counts for 0.4 of scan time at each end of scan
Temperature	22 ± 1 °C
Standard reflections	333, 33$\bar{3}$, 3$\bar{3}\bar{3}$
Number of reflections collected between checks	125
Unique data measured	696
Observed data, n	443 ($>3\sigma_F$)
Number of variables, p	72
$R_F = \Sigma \|\|F_o\| - \|F_c\|\| / \Sigma \|F_o\|$	0.086
$R_w = [\Sigma w(\|F_o\| - \|F_c\|)^2 / \Sigma w\|F_o\|^2]^{1/2}$	0.101
Weighting scheme	$w = [\sigma_F{}^2(\|F_o\|) + 0.003\|F_o\|^2]^{-1}$
Largest shift in the last cycle	0.01
Goodness of fit, S	1.305
F(000)	4766.67 eA^{-3}

tion using D,L-penicillamine yielded crystals giving the same X-ray diffraction pattern, indicating that identical or enantiomorphous crystals were obtained. *Anal.* Calcd. for $C_{30}H_{72}Cl_8Hg_6N_6O_{17}S_6$: C, 14.08; H, 3.23; N, 3.28. Found: C, 14.60; H, 3.08; N, 3.43%.

The bromo-analog was prepared in the same way by the reaction of mercuric bromide with D,L-penicillamine or D-penicillamine. X-Ray photographs confirmed that it is iso-structural with the chloro-analog. *Anal.* Calcd. for $C_{30}H_{72}Br_8Hg_6N_6O_{17}S_6$: C, 12.36; H, 2.84; N, 2.88; Br, 21.94. Found: C, 11.87; H, 2.74; N, 2.92; Br, 22.04%.

Crystallographic Study

Preliminary Weissenberg and precession photographs suggested cubic space group $P4_132$ (O^7), No. 213; systematic absences: $h00$, $h \neq 4n$) which was further confirmed by the Harker peaks on a Patterson map [6]. Another fresh crystal was mounted on a Nicolet R3m automated four-circle diffractometer. Accurate unit-cell dimensions were determined from a least-squares fit of 22 reflections ($11° < 2\theta < 19°$; Mo-Kα radiation). The reflection intensities declined rapidly with increasing Bragg angle, and data were collected in the range $0° < 2\theta < 45°$. Three standards monitored every 125 reflections showed only small random fluctuations within ±1%, and linear scaling was applied. In addition to Lorentz and polarization factors, absorption correction was also applied using an empirical method based on a pseudo-ellipsoidal treatment of intensity measurements of selected strong reflections at different azimuthal angles. Other data collection and processing details are listed in Table I.

A sharpened Patterson map readily revealed the position of the Hg atom in the molecule. Other non-hydrogen atoms were located on subsequent difference Fourier maps. Anisotropic thermal parameters for the Hg, Cl, and S atoms and isotropic thermal parameters for the O, N, and C atoms were varied. Blocked-cascade least-squares refinement converged at R_F = 0.086 for 443 observed reflections. In view of the serious X-ray absorption of the crystal, no attempt was made to assign positions for

TABLE II. Fractional Coordinates ($\times 10^{-3}$) and Isotropic Thermal Parameters[a] ($Å^2 \times 10^{-2}$) of all Non-hydrogen Atoms.

Atom	Site Symmetry	x	y	z	U_{iso}/U_{eq}
Hg	1	78.0(2)	109.2(2)	226.6(2)	8.1(3)
Cl(1)	2	125	−46(1)	204(1)	10(3)
Cl(2)	2	125	471(1)	721(1)	7(2)
Cl(3)	3	173(1)	173	173	7(1)
S	1	−4(1)	54(1)	303(1)	6(1)
O(1)	1	−189(3)	225(3)	375(3)	10(2)
O(2)	1	−93(2)	281(2)	398(2)	6(1)
O(3)	2	125	284(3)	534(3)	12(3)
O(4)	3	53(2)	53	53	4(2)
N	1	−140(3)	138(3)	269(3)	8(2)
C(1)	1	−122(4)	228(3)	369(3)	9(2)
C(2)	1	−85(3)	178(3)	315(3)	3(1)
C(3)	1	−42(3)	121(3)	357(3)	5(2)
C(4)	1	23(3)	163(4)	404(3)	6(2)
C(5)	1	−90(4)	80(5)	414(4)	10(3)

[a]Form of isotropic temperature factor: $\exp(-8\pi^2 U_{iso}\sin^2\theta/\lambda^2)$. U_{eq} calculated as one-third of the orthogonalized U matrix.

TABLE III. Bond Distances (A) and Angles (deg).

$[Cl\{HgSC(CH_3)_2CH(NH_3)COO\}_3]^{2+}$ trinuclear moiety					
Hg–Cl(3)	2.37(1)	Hg–Cl(3)–Hg′	98.5(9)	C(1)–C(2)–C(3)	109(2)
Hg–S	2.32(2)	Cl(3)–Hg–S	167.2(9)	O(1)–C(1)–O(2)	116(6)
S–C(3)	1.77(6)	Hg–S–C(3)	108(2)	O(1)–C(1)–C(2)	119(6)
C(3)–C(2)	1.54(8)	S–C(3)–C(2)	114(4)	O(2)–C(1)–C(2)	124(6)
C(3)–C(4)	1.68(9)	S–C(3)–C(4)	110(4)	Hg···Cl(1)···Hg″	79.6(7)
C(3)–C(5)	1.59(10)	S–C(3)–C(5)	105(4)	Cl(1)···Hg–Cl(3)	101.9(3)
C(2)–N	1.54(8)	C(2)–C(3)–C(4)	109(5)	Cl(1)···Hg–S	81.6(5)
C(2)–C(1)	1.54(8)	C(2)–C(3)–C(5)	112(5)		
C(1)–O(1)	1.25(9)	C(4)–C(3)–C(5)	106(5)		
C(1)–O(2)	1.25(8)	N–C(2)–C(1)	111(5)		
Hg···Cl(1)	3.06(2)	N–C(2)–C(3)	108(4)		
Weak interactions and hydrogen bonding					
Hg···O(4)	3.44(5)				
O(2)···O(2′)	2.24(8)	C(1)–O(2)···O(2′)	119(4)		
Cl(2)···O(3)	2.46(4)	O(3)···Cl(2)···O(3′)	115(4)	Cl(2)···O(3)···Cl(2′)	125(4)

the hydrogen atoms. The final difference map contained residual peaks in the neighbourhood of the Hg and S atoms, with extrema in the range 1.0 to -1.1 eÅ^{-3}.

All computations were performed on a Data General Corporation Nova 3/12 minicomputer with the SHELXTL program package [7, 8]. Analytical expressions [9] of neutral atomic scattering factors [10] were employed, and anomalous dispersion corrections [11] were incorporated. The final positional and isotropic thermal parameters are given in Table II. Tables of anisotropic thermal parameters for the Hg, Cl, and S atoms and observed and calculated structure factors have been deposited at the Editorial Office in Padua.

Results and Discussion

For structural reasons the title compound is best formulated as $2[(\mu_3\text{-Cl})\{Hg(penH)\}_3]^{2+}\cdot 2H_3O^+\cdot 3(\mu_2\text{-Cl})^-\cdot(H_2O\cdot Cl^-)_3$, where penH designates the penicillaminato ligand $[SC(CH_3)_2CH(NH_3)COO]^-$. Bond distances and angles are given in Table III in accordance with the atomic labelling in Fig. 1.

In the crystal lattice three crystallographically equivalent $[Hg(penH)]^+$ units are symmetrically linked by a triply bridging chloride ion [strong Hg–Cl(3) bond of lengths 2.37(1) Å; Hg–Cl(3)–Hg′ = 98.5(9)°]. Each of these pyramidal trinuclear $[(\mu_3\text{-Cl})\{Hg(penH)\}_3]^{2+}$ moieties (Fig. 1) interacts with three others through moderately strong sym-

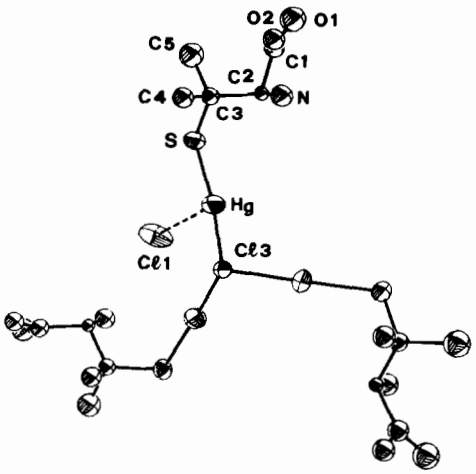

Fig. 1. A perspective view of the $[(\mu_3\text{-Cl})\{HgSC(CH_3)_2CH(NH_3)COO\}_3]^{2+}$ unit, including one of the doubly bridging chloride ligands. The atom labelling scheme corresponds to that of Table II.

metrical chloride bridges [Hg–Cl(1) = 3.06(2) Å; Hg–Cl(1)–Hg″ = 79.6(7)°], forming a three-dimensional network. The carboxylate groups of two neighboring penicillamine ligands are strongly linked *via* a symmetrical O···H···O hydrogen bond, whose length of 2.24(8) Å is comparable to those reported in the literature [1, 12–14]. The hydrogen bonding scheme is also consistent with the observed carboxyl vibration modes [ν(C=O) 1740 (s, br); ν(C–O) 1300 cm^{-1} (m, br)]. The protons involved in this type of hydrogen bonding come from half of the amino groups. Thus on the average, 2½ protons reside on each amino group in the unit cell. This kind of disordering is supported by the observed vibrational frequencies [$\delta_{as}(-NH_3^+)$ 1570 (w, br); $\delta_s(-NH_3^+)$ 1480 cm^{-1} (w, sh)] [6] which are lower than those for penicillamine hydrochloride [$\delta_{as}(-NH_3^+)$ 1624(m); $\delta_s(-NH_3^+)$ 1520 cm^{-1} (s)] [15] but higher than those for the N-bonded complexes $(CH_3Hg)_2$(pen) [$\delta_{as}(-NH_2^+-)$ 1586(vs); $\delta_s(-NH_2^+-)$ 1230 cm^{-1} (w, sh)] [16] and CH_3Hg(D,L-methionine) [$\delta_{as}(-NH_2^+-)$ 1590 (vs, br); $\delta_s(-NH_2^+-)$ 1250 cm^{-1} (m, br)] [17].

Hydrogen bonding between Cl(2) and the water molecules of crystallisation forms planar six-membered $(H_2O\cdot Cl^-)_3$ rings of edge O(3)–H···Cl(2) = 2.46(4) Å. These strongly hydrogen bonded rings fill the voids of the three-dimensional network constructed by $[Hg(penH)]^+$, Cl(1), and Cl(3) (molecular packing shown in Fig. 2), with no interatomic contact less than 4 Å between the two components. To our knowledge the $(H_2O\cdot Cl^-)_3$ ring is novel and constitutes a higher homolog of the recently discovered planar cyclic hydrogen-bonded $(H_2O\cdot Br^-)_2$ system in crystalline $[(CH_2)_6N_4CH_3]Br\cdot H_2O$ [18]. Atom O(4) occupies a site of symmetry 3 and only weakly interacts with Hg [Hg···O(4) = 3.44(5) Å]. To preserve overall electroneutrality in the crystal, O(4) is identified with the hydronium (or oxonium) ion H_3O^+.

The coordination around the Hg atom is mainly diagonal with significant distortion from linearity [Cl(3)–Hg–S = 167.2(9)°]. The strong Hg–X bonds [Hg–Cl(3) = 2.37(1) and Hg–S = 2.32(2) Å] are comparable to those in similar diagonal S–Hg–X (X = S, Cl) systems such as the L-cysteine complex $Hg(cystH_2)(cystH)Cl\cdot\frac{1}{2}H_2O$ [Hg–S = 2.353(3) and 2.329(5) Å] [1], where cystH stands for the L-cysteinato ligand $[SCH_2CH(NH_3)COO]^-$, or the D,L-penicillamine complexes $[Hg(penH_2)_2Cl]Cl\cdot H_2O$ [Hg–S = 2.335(5) and 2.357(4) Å] and $(HgCl_2)_2\cdot(penH_2)\cdot 2H_2O$ [Hg(2)–S = 2.356(5) and Hg(2)–Cl(4) = 2.356(5) Å] [2]. All these Hg–X bonds are distinctly shorter than corresponding bonds in the tetrahedrally coordinated L-cysteine complex $HgCl_2(cystH_2)$ [Hg–S = 2.453(4) and 2.490(4); Hg–Cl = 2.582(4) and 2.645(5) Å] [1].

The linearity of the S–Hg–X units is susceptible to distortion by weaker interactions with other ions. The Cl(3)–Hg–S angle in the present 1:1 complex $2[Cl\{Hg(penH)\}_3]\cdot 3Cl\cdot 2H_3O\cdot(H_2O\cdot Cl)_3$ deviates by 12.8° from 180° because of the participation of Cl(1) in the primary coordination shell around Hg. While the chloride ions are excluded from the primary coordination shell in the 1:2 $HgCl_2/cystH_2$ complex [Hg···Cl = 3.232(5) Å], they interact strongly with Hg atoms in the 1:1 complex [1].

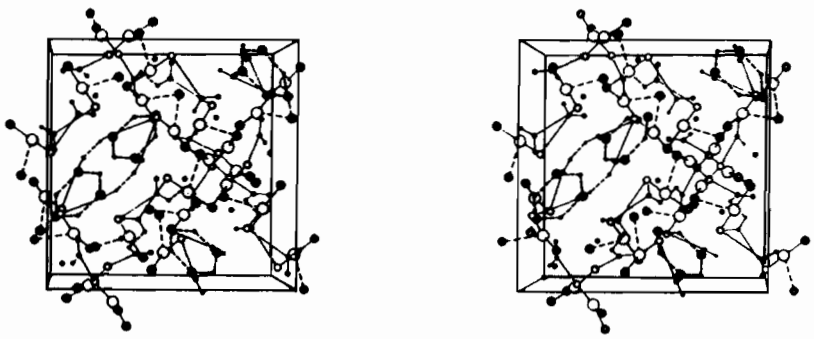

Fig. 2. Packing and hydrogen bonding in $2[(\mu_3\text{-Cl})\{Hg(penH)\}_3]\cdot 3(\mu_2\text{-Cl})\cdot 2(H_3O)\cdot(H_2O\cdot Cl)_3$. For clarity, the $-(CH_3)_2CH(NH_3)-$ fragment is represented by a line linking S with C(1) of the carboxylate group.

TABLE IV. Torsion Angles (deg) in the D-penicillamine Skeleton.[a]

O(1)=C(1)–C(2)–N, $\psi_T{}^1$	9(8)	C(1)–C(2)–C(3)–S	174(4)
O(1)=C(1)–C(2)–C(3)	–110(7)	C(1)–C(2)–C(3)–C(4)	–63(6)
O(2)–C(1)–C(2)–N, $\psi_T{}^2$	–158(6)	C(1)–C(2)–C(3)–C(5)	54(7)
O(2)–C(1)–C(2)–C(3)	83(7)	C(2)–C(3)–S–Hg	63(4)
N–C(2)–C(3)–S, χ^1	54(6)	C(4)–C(3)–S–Hg	–59(4)
N–C(2)–C(3)–C(4)	176(4)	C(5)–C(3)–S–Hg	–173(4)
N–C(2)–C(3)–C(5)	–66(6)		

[a]Notations $\psi_T{}^1$, $\psi_T{}^2$, and χ^1 follow the convention in: IUPAC-IUB Commission on Biochemical Nomenclature, *J. Mol. Biol.*, *52*, 1 (1970).

The same trend is also found for the $HgCl_2/penH_2$ complex series but with even stronger metal-chloride interactions. Hence the participation of chloride ions in the primary coordination shell increases as the $Hg/penH_2$ ratio in the compound decreases. The 1:2 complex $[Hg(penH_2)_2Cl]Cl\cdot H_2O$ consists mainly of two-coordinate S–Hg–S with a moderately strong Hg–Cl bond [Hg–Cl(1) = 2.850(5); also weak interaction Hg···Cl(1′) = 3.323(5) Å] [2]. One of these two Hg–S bonds is replaced by a very strong Hg–Cl bond [2.37(1) Å; Cl triply bridging] with retention of the moderately strong Hg–Cl bond [3.06(2) Å] in the present 1:1 complex, whereas the $[ClHgSC(CH_3)_2CH(NH_3)COOH]^+$ moiety in the 2:1 complex $(HgCl_2)_2(penH_2)\cdot 2H_2O$ consists of a distorted linear S–Hg–Cl system with four bridging chloride interactions [Hg–Cl in the range 2.780(5)–3.429(5) Å] [2]. Thus from the structural point of view the conversion of one $HgCl_2/penH_2$ complex to another can be rationalised in the following way. Replacement of a penicillamine ligand in the 1:2 complex with a chloride ion gives the 1:1 complex, and the 2:1 complex can be regarded as an adduct of $HgCl_2$ with the 1:1 complex. In fact, an nmr study has provided evidence for the interconversion of $Hg^{2+}/penH_2$ complexes in solution [6].

Due to the weak diffracting power of crystalline $2[Cl\{Hg(penH)\}_3]\cdot 3Cl\cdot 2H_3O\cdot(H_2O\cdot Cl)_3$ and the predominate scattering of the heavy Hg atom, it has not been possible to determine the bond distances for the penicillamine skeleton with good precision. They are all in reasonable agreement, within experimental errors, with corresponding values found in the free base [15], as well as in its hydrochloride [19] or complexes like $[Hg(penH_2)_2Cl]Cl\cdot H_2O$, $(HgCl_2)_2(penH_2)\cdot 2H_2O$ [2, 3], and [Co(L-histidine)-(D-penH)]·H_2O [20]. However, the penicillamine ligand adopts different conformations in these compounds. Torsion angles of interest for the D-penicillamine skeleton in the present complex is listed in Table IV. The torsion angle C(1)–C(2)–C(3)–S = 174(4)° indicates that the bulky sulfur atom is anti-periplanar to the carboxyl terminus. This is a characteristic conformation for compounds with protonated carboxylate groups. In those compounds like meso-penicillamine [15], $CH_3Hg(penH)\cdot H_2O$, and $(CH_3Hg)_2(pen)$ [16], where intramolecular interactions bend the skeleton to form six-membered rings [O–C(1)–C(2)–C(3)–S–M, M = Hg or H], the bulky sulfur atoms are ±synclinal to the deprotonated carboxylate groups and are located between the comparatively large amino and carboxyl groups, resulting in higher conformation energies. Further twisting of the penicillamine skeleton is observed for tridentate ligands such as in the S,N,O-bonded complex [Co(L-histidine)(D-penH)]·H_2O [20]. Another intramolecular interaction in the present complex, namely the possible hydrogen bonding between the amino and carboxyl groups [N···O(1) 2.71(8) Å], leads to torsion angles O(1)=C(1)–C(2)–N ($\psi_T{}^1$) and O(2)–C(1)–C(2)–N ($\psi_T{}^2$) of 9(8) and –158(6)° respectively, in contrast to those [–21.2 to –23.6 and 156.4 to 164.5° respectively] for L-$penH_2\cdot HCl\cdot H_2O$ [19], $[Hg(penH_2)_2Cl]Cl\cdot H_2O$, and $(HgCl_2)_2$-$(penH_2)\cdot 2H_2O$ [2, 3], where the amino groups are in the proximity of the carbonyl oxygen atoms.

It has been found that the complex $[Ni(D\text{-}pen)_2]^{2-}$ is thermodynamically more stable than $[Ni(D\text{-}pen)(L\text{-}pen)]^{2-}$ [21]. The enantiomorphous crystallisation observed in the present 1:1 $HgCl_2/penH_2$ system provides an interesting example of stereochemical selectivity, which may be contrasted wih the reaction of $CoCl_2\cdot 2H_2O$ with D,L-histidine followed by addition of D,L-penicillamine to yield crystalline [Co(L-his)(D-pen)] [Co(D-his)(L-pen)]·$2H_2O$ [22].

Acknowledgement

The authors wish to thank Professors A. J. Carty and C. Chieh (University of Waterloo, Ontario, Canada) for their interest and advice.

References

1 N. J. Taylor and A. J. Carty, *J. Am. Chem. Soc., 99,* 6143 (1977).
2 A. J. Carty and N. J. Taylor, *J. Chem. Soc., Chem. Commun.,* 214 (1976).
3 A. J. Carty and N. J. Taylor, unpublished results.
4 L. Lander, *Nature, 230,* 452 (1971).
5 A. Jernelov, in 'Mercury, Mercurials and Mercaptans', M. W. Miller and T. W. Clarkson, eds., Thomas Books, Springfield, Ill., pp. 315–324 (1973).
6 L. Book, Ph.D. Thesis, University of Waterloo (1980).
7 G. M. Sheldrick, SHELXTL. Crystal structure determination system: Revision 3A, Nicolet XRD Corp., Fremont, Calif. (1981).
8 G. M. Sheldrick, in 'Computational Crystallography', D. Sayre, ed., Oxford University Press, New York, p. 506 (1982).
9 D. T. Cromer and J. B. Mann, *Acta Cryst., A24,* 321 (1968).
10 'International Tables for X-Ray Crystallography', Vol. IV, Kynoch Press, Birmingham, p. 99 (1973).
11 Ref. 10, p. 149.
12 W. H. Hamilton and J. A. Ibers, 'Hydrogen Bonding in Solids', W. A. Benjamin, New York (1968).
13 S. N. Vinogradov and R. H. Linnell, 'Hydrogen Bonding', Van Nostrand Reinhold, New York (1971).
14 L. Book, A. J. Carty and C. Chieh, *Can. J. Chem., 59,* 138 (1981).
15 H. E. Howard-Lock, C. J. L. Lock and P. S. Smalley, *J. Cryst. Spectrosc. Res., 13,* 333 (1983).
16 Y. S. Wong, A. J. Carty and C. Chieh, *J. Chem. Soc. Dalton,* 1801 (1977).
17 Y. S. Wong, A. J. Carty and P. C. Chieh, *J. Chem. Soc. Dalton,* 1157 (1977).
18 T. C. W. Mak, *Inorg. Chem., 23,* 620 (1984).
19 S. N. Rao, R. Pathasarathy and F. E. Cole, *Acta Cryst., B29,* 2373 (1973).
20 P. de Meester and D. J. Hodgson, *J. Am. Chem. Soc., 99,* 101 (1977).
21 J. H. Ritsma and F. Jellinek, *Rec. Trav. Chim., 91,* 923 (1972).
22 P. de Meester and D. J. Hodgson, *J. Chem. Soc., Chem. Commun.,* 280 (1976).