

Table S–1. IR Data and Tentative Assignments for the ReOX₂(met) Complexes.

	D-met	ReOCl ₂ -(D-met)	ReOBr ₂ -(D,L-met)	ReOCl ₂ -(D,L-met)	D,L-met
$\nu(\text{NH}_3^+)$	~3000 s, br				~3000 s, br
$\nu_a(\text{NH}_2)$		3237 s	3228 w	3230 w	
$\nu_s(\text{NH}_2)$		3139 s	3175 w	3180 w	
$\nu(\text{CH})$	2917 w	2924 w	2927 w	2929 w	
$\nu(\text{OH})$ (CH ₃ OH)			3063 m	3054 m	
					1657 m
$\nu_a(\text{CO}_2)/\nu(\text{C=O})$	1618 s	1719 vs 1704 vs	1680 vs	1685 vs	1625 s 1610 s
$\beta_a(\text{NH}_3^+)/\beta_a(\text{NH}_2)$	1586 s 1561 s	1596 w	1619 m	1620 m	1581 vs
$\beta_s(\text{NH}_3^+)$	1512 s				1515 m
$\beta(\text{CH}_3)/\beta(\text{OH})$ (CH ₃ OH)			1446 w	1446 w	
$\beta(\text{CH}_2)$	1450 w	1437 m	1429 m	1429 m	1450 w
$\beta(\text{CH}_3)$	1422 sh	1422 m	1415 sh	1415 sh	
$\nu_s(\text{CO}_2)/\nu(\text{C-O})$	1409 s	1374 m	1361 m	1364 m	1414 s
$\beta(\text{CH}_3)$	1352 m	1338 w	1347 m	1349 m	1341 s
$\beta(\text{CH})/\beta(\text{CH}_2)$	1334 w 1322 m	1322 w			1314 m
$\beta(\text{CH})/\beta(\text{CH}_2)$	1276 w 1268 w	1300 m 1274 s	1293 s 1274 m	1296 s 1277 m	1275 m
$\beta(\text{CH})/\beta(\text{CH}_2)$	1243 m	1249 w	1213 m	1216 m	1219 m
$\beta(\text{CH}_2)$	1184 w 1174 w	1198 m 1174 m	1192 m 1177 s	1192 m 1181 m	
$\beta(\text{CH})/\nu(\text{CN})$	1151 m	1151 s	1146 m	1148 m	1159 m
		1103 vw			1103 w
$\nu(\text{CC})/\rho(\text{NH}_3^+)$	1071 w	1088 vw	1086 w	1085 w	1080 m
$\nu(\text{CC})$	1028 w		1041 w	1045 w	1047 w
$\rho(\text{CH}_2) / \nu(\text{C-O})$ (CH ₃ OH)	1006 w	1016 w	1008 w	1009 w	999 m
$\nu(\text{Re=O})$		996 vs	993 vs	995 vs	
$\rho(\text{NH}_3^+)/\rho(\text{NH}_2)$	982 m	975 m	974 m	975 m	
$\rho(\text{CH}_3)$	953 m	966 m 917 m	956 m 933 m	957 s 934 m	955 m
$\rho(\text{NH}_3^+)$	926 w				930 m
$\nu(\text{CC})/\beta(\text{CO}_2)$	878 s	878 w	883 m	884 m	877 m
$\rho(\text{NH}_3^+)/\nu(\text{CC})$	808 s	840 w	845 m	846 m	
$\beta(\text{CO}_2)$	768 m	786 m	800 w	802 w	780 m
$\nu_a(\text{SC})$	752 m	765 w	752 m	754 m	755 m
	724 w 712 w		722 w	726 w	719 m
$\rho(\text{CH}_2)$	684 m	731 w	696 w	696 w	685 m
	662 w				
$\nu_s(\text{SC})$	648 m	648 vw	678 w	680 w	650 w
$\rho(\text{CO}_2)$	548 vs	591 m	615 s	617 vs	553 vs

The modes are labeled according to the convention of ref ¹: ν , stretching; β , bending; ρ , all other deformations.

The spectrum of methionine has been discussed in detail by Cao and Fischer.¹ Those of the complexes have been tentatively assigned by considering the trends noted upon Re/Tc complexation to related amino acids^{2,3} and the influence of protonation in cationic methionine.⁴

The strong Re=O stretching mode is found at $\sim 995\text{ cm}^{-1}$. Coordination of the carboxylate group shifts the $\nu_a(\text{CO}_2)$ mode ($\sim 1620\text{ cm}^{-1}$) to $1685\text{--}1710\text{ cm}^{-1}$. The $\nu_s(\text{CO}_2)$ counterpart is displaced to a lesser extent, from ~ 1410 to $\sim 1366\text{ cm}^{-1}$, in the opposite direction as expected. The complexes also show strong bands at 591 (D-met) or 617 cm^{-1} (D,L-met), believed to correspond to a carboxylate deformation mode shifted from ($\sim 550\text{ cm}^{-1}$) upon complexation. Similar trends have been noted for the corresponding histidine compounds.²

The coordinated amino group introduces distinctive features. The very strong and broad band centered at $\sim 3000\text{ cm}^{-1}$ for the free ligand is replaced by better defined asymmetric and symmetric NH_2 stretching modes at $\sim 3235\text{ cm}^{-1}$ and $\sim 3160\text{ cm}^{-1}$, respectively. The NH_2 deformation mode gives weaker features near 1600 cm^{-1} , whereas the remaining NH_2 vibrations have not been identified with certainty. No clear diagnostic for thioether coordination can be extracted from the IR spectra. The $\nu_a(\text{S-C})$ and $\nu_s(\text{S-C})$ vibrations are believed to appear at 752 and 648 cm^{-1} , respectively, in free methionine.¹ The higher-energy vibration is not shifted by complexation, whereas interference with the $\rho(\text{CH}_2)$ mode makes it difficult to identify the weak bands in the $600\text{--}700\text{ cm}^{-1}$ region.

Complexes **1** and **3** also exhibit vibrations from lattice methanol at ~ 3060 and 1446 cm^{-1} .

Table S–2. Selected Bond Angles ($^{\circ}$) in the Methionine Complexes.

	1a	2	3	3a
O=Re–O	163.9(2); 166.5(2); 166.3(2)	164.7(2)	161.7(4); 161.9(5)	163.3(4); 161.6(3)
S–Re–X(1)	172.08(7); 171.62(5); 167.07(6)	168.83(6)	169.3(1); 165.7(1)	167.20(7); 165.80(8)
N–Re–X(2)	162.2(1); 162.2(1); 162.1(2)	164.8(2)	162.3(4); 164.0(3)	162.9(2); 163.8(2)
N–Re–O	74.3(2); 75.0(2); 75.2(2)	75.1(2)	73.7(5); 73.2(4)	74.2(3); 74.0(3)
S–Re–O	84.7(1); 86.2(1); 83.1(1)	84.6(2)	78.5(3); 79.3(3)	79.1(2); 78.7(2)
X(1)–Re–O	87.5(1); 86.7(1); 84.1(1)	84.3(2)	90.7(3); 86.8(2)	88.1(2); 87.3(2)
X(2)–Re–O	88.4(1); 87.5(1); 87.1(1)	89.9(1)	88.6(3); 90.8(3)	88.7(2); 89.9(2)
N–Re=O	91.2(2); 91.8(2); 92.3(2)	89.9(2)	92.4(5); 91.2(5)	92.6(4); 90.8(4)
S–Re=O	88.9(2); 90.1(2); 91.2(2)	92.3(2)	89.8(4); 91.9(4)	90.9(3); 91.3(3)
X(1)–Re=O	98.3(2); 95.9(2); 101.0(2)	98.6(2)	100.6(3); 102.4(4)	101.6(3); 102.8(3)
X(2)–Re=O	106.5(2); 105.8(2); 105.6(2)	105.2(2)	105.2(4); 104.7(4)	104.4(3); 105.3(3)
X(1)–Re–X(2)	89.36(8); 88.84(7); 88.62(7)	86.70(7)	91.89(6); 89.59(7)	91.40(5); 89.86(6)
S–Re–N	90.7(1); 87.0(1); 88.7(1)	88.1(2)	90.0(3); 90.1(3)	89.8(2); 90.4(2)
S–Re–X(2)	91.75(7); 95.22(6); 92.24(6)	92.85(6)	87.7(1); 87.4(1)	87.92(8); 88.08(9)
N–Re–X(1)	85.9(1); 87.0(2); 86.6(1)	89.4(2)	87.1(3); 88.9(3)	87.1(2); 87.7(2)
C(1)–O–Re	122.2(4); 123.4(4); 120.9(4)	122.6(4)	119.8(10); 122.0(9)	119.6(7); 120.9(6)
C(5)–S–C(4)	100.1(4); 98.9(3); 99.5(4)	98.7(3)	102.0(9); 102.5(9)	102.1(7); 102.6(7)
C(5)–S–Re	111.6(3); 114.0 (3); 111.0(3)	110.6(3)	106.7(5); 108.4(7)	107.1(4); 106.5(6)
C(4)–S–Re	107.2(2); 107.1(2); 109.1(2)	107.4(2)	101.4(5); 101.0(5)	101.4(4); 101.1(4)
C(2)–N–Re	110.6(3); 111.6(4); 111.4(3)	110.9(4)	109.1(8); 109.7(8)	109.8(6); 110.8(6)

Table S–3. Distances from Least-squares Planes in the Methionine Complexes.

1a, molecule 1	1a, molecule 2	1a, molecule 3	2
Plane defined by Re, S, C3, C2			
0.060(2) Re1*	0.027(2) Re2*	-0.046(2) Re3*	0.032(2) Re*
-0.064(2) S1*	-0.029(3) S2*	0.048(2) S3*	-0.034(2) S*
0.099(3) C13*	0.045(4) C23*	-0.076(3) C33*	0.052(3) C3*
-0.095(3) C12*	-0.044(4) C22*	0.074(3) C32*	-0.050(3) C2*
-0.663(9) C14	-0.643(9) C24	-0.594(8) C34	-0.670(8) C4
0.822(6) N1	0.882(6) N2	0.844(6) N3	0.879(6) N
Plane defined by S, C4, C2, N			
-0.070(2) S1*	-0.074(3) S2*	0.086(2) S3*	-0.069(2) S*
0.091(3) C14*	0.092(3) C24*	-0.108(3) C34*	0.087(3) C4*
-0.109(4) C12*	-0.111(4) C22*	0.130(3) C32*	-0.104(3) C2*
0.089(3) N1*	0.092(3) N2*	-0.108(3) N3*	0.087(3) N*
0.732(8) C13	0.665(9) C23	-0.667(9) C33	0.695(9) C3
-1.092(6) Re1	-1.199(6) Re2	1.101(6) Re3	-1.189(6) Re
Plane defined by Re, N, C3, C4			
0.005(2) Re1*	-0.031(2) Re2*	0.026(2) Re3*	-0.022(2) Re*
-0.007(3) N1*	0.045(3) N2*	-0.037(3) N3*	0.031(3) N*
0.009(4) C13*	-0.058(5) C23*	0.047(4) C33*	-0.040(4) C3*
-0.007(3) C14*	0.045(4) C24*	-0.036(3) C34*	0.031(3) C4*
0.853(6) S1	0.922(7) S2	-0.821(6) S3	0.921(6) S
-0.806(7) C12	-0.796(8) C22	0.785(8) C32	-0.796(8) C2
Plane defined by Re, N, C1, O2			
0.058(2) Re1*	0.031(2) Re2*	-0.022(2) Re3*	0.021(3) Re*
-0.042(1) N1*	-0.022(1) N2*	0.017(1) N3*	-0.016(2) N*
0.081(2) C11*	0.042(3) C21*	-0.031(3) C31*	0.030(3) C1*
-0.097(3) O12*	-0.051(3) O22*	0.036(3) O32*	-0.036(4) O2*
0.518(8) C12	0.506(9) C22	-0.524(8) C32	0.533(9) C2
3, molecule 1	3, molecule 2	3a, molecule 1	3a, molecule 2
Plane defined by Re, S, C3, C2			
-0.140(6) Re1*	-0.126(5) Re2*	-0.121(4) Re1*	-0.121(4) Re2*
0.145(6) S1*	0.135(6) S2*	0.129(4) S1*	0.130(4) S2*
0.229(8) C12*	0.205(8) C22*	0.200(5) C12*	0.200(6) C22*
-0.234(8) C13*	-0.215(8) C23*	-0.207(6) C13*	-0.209(6) C23*
-0.82(2) C14	-0.89(2) C24	-0.86(1) C14	-0.88(1) C24
-0.70(2) N1	-0.71(2) N2	-0.72(1) N1	-0.70(1) N2

* Atoms used to define planes

Table S–4. Torsion Angles ($^{\circ}$) in the Chelate Rings of the Methionine Complexes.

	1a*	2	3	3a
Re-S-C4-C3	-49.5(5); -49.7(6); -45.1(6)	-51.0(5)	-67.7(10); -71.0(12)	-69.3(7); -69.7(7)
S-C4-C3-C2	67.2(6); 60.9(8); 58.2(7)	62.4(7)	46.9(16); 53.7(18)	52.3(12); 53.6(12)
C4-C3-C2-N	-84.3(6); -76.7(8); -78.0(7)	-78.3(7)	38.8(18); 31.7(19)	32.3(13); 29.4(14)
C3-C2-N-Re	79.7(5); 82.4(5); 82.5(5)	81.4(5)	-86.7(11); -83.2(12)	-84.2(8); -82.1(9)
C2-N-Re-S	-55.5(3); -61.7(4); -58.2(4)	-59.9(4)	44.4(9); 44.8(8)	45.3(6); 44.7(6)
N-Re-S-C4	40.0(3); 43.8(3); 39.7(3)	44.1(3)	19.8(7); 21.4(7)	19.1(5); 20.6(5)
Re-N-C2-C1	-39.2(5); -37.1(5); -38.7(5)	-38.3(6)	36.8(13); 39.4(12)	38.0(8); 39.3(9)
N-C2-C1-O2	29.1(6); 31.6(7); 35.1(7)	35.0(8)	-17.5(17); -21.3(15)	-20.2(11); -22.7(11)
C2-C1-O2-Re	-5.0(6); -12.0(7); -15.5(7)	-15.8(9)	-12.9(16); -8.9(15)	-9.0(11); -5.5(10)
C1-O2-Re-N	-13.6(4); -7.2(5); -5.1(4)	-5.1(6)	26.6(10); 24.9(9)	24.3(7); 22.2(7)
O2-Re-N-C2	28.8(3); 25.1(4); 25.0(4)	25.0(4)	-33.6(9); -34.0(8)	-33.5(6); -33.4(6)

*The sign of the torsion angles calculated from the refined coordinates has been changed to describe a complex containing a D–met ligand, for consistency with the other compounds

Table S–5. Geometry of the Hydrogen Bonds in the Methionine Complexes.

	<i>D</i> –H (Å)	H··· <i>A</i> (Å)	<i>D</i> ··· <i>A</i> (Å)	<i>D</i> –H··· <i>A</i> (°)
Complex 1a				
N1–H1A···O33 ^a	0.90	2.52	3.122(7)	124.8
N1–H1A···Cl22 ^b	0.90	2.77	3.490(5)	137.5
N1–H1B···O32 ^a	0.90	2.11	2.893(6)	145.3
N2–H2A···O33 ^c	0.90	2.02	2.810(7)	146.6
N2–H2B···Cl21 ^d	0.90	2.50	3.362(5)	160.8
N3–H3A···O23	0.90	2.06	2.900(7)	154.2
N3–H3B···O13 ^e	0.90	1.93	2.831(7)	178.4
Complex 2				
N–H1A···Cl2 ^c	0.90	2.74	3.547(5)	150.2
N–H1A···Cl1 ^c	0.90	2.93	3.655(5)	139.2
N–H1B···O3 ^f	0.90	2.00	2.797(8)	146.7
Complex 3a				
N1–H1A···O1	0.90	2.35	3.094(12)	140.2
N1–H1A···Br21	0.90	3.11	3.671(8)	122.1
N1–H1B···O23 ^g	0.90	2.05	2.943(12)	171.9
N1–H1B···O22 ^g	0.90	2.54	3.057(11)	116.7
N2–H2A···O1	0.90	2.13	2.960(13)	152.0
N2–H2B···O13 ^h	0.90	2.05	2.938(12)	169.6
O1–H1C···Br21 ^g	0.82(4)	2.77(3)	3.462(10)	144(4)
O1–H1D···Br11 ^h	0.82(4)	2.78(4)	3.595(10)	177(5)
Complex 3				
N1–H1A···O1	0.90	2.21	2.981(17)	143.2
N1–H1A···Br21	0.90	3.09	3.714(11)	128.4
N1–H1B···O23 ^g	0.90	2.04	2.929(18)	167.4
N1–H1B···O22 ^g	0.90	2.64	3.141(15)	116.0
N2–H2A···O1	0.90	2.03	2.902(15)	163.0
N2–H2B···O13 ^h	0.90	2.10	2.961(17)	160.3
O1–H1C···Br21 ^g	0.82	2.52	3.299(14)	159.0

^a –x+1, –y+2, –z+1; ^b x, –y+³/₂, z–¹/₂; ^c x–1, y, z; ^d –x, y+¹/₂, –z+³/₂; ^e –x+1, –y+1, –z+1; ^f –x+1, y+¹/₂, –z+³/₂; ^g –x+1, –y+1, –z; ^h –x, –y+1, –z

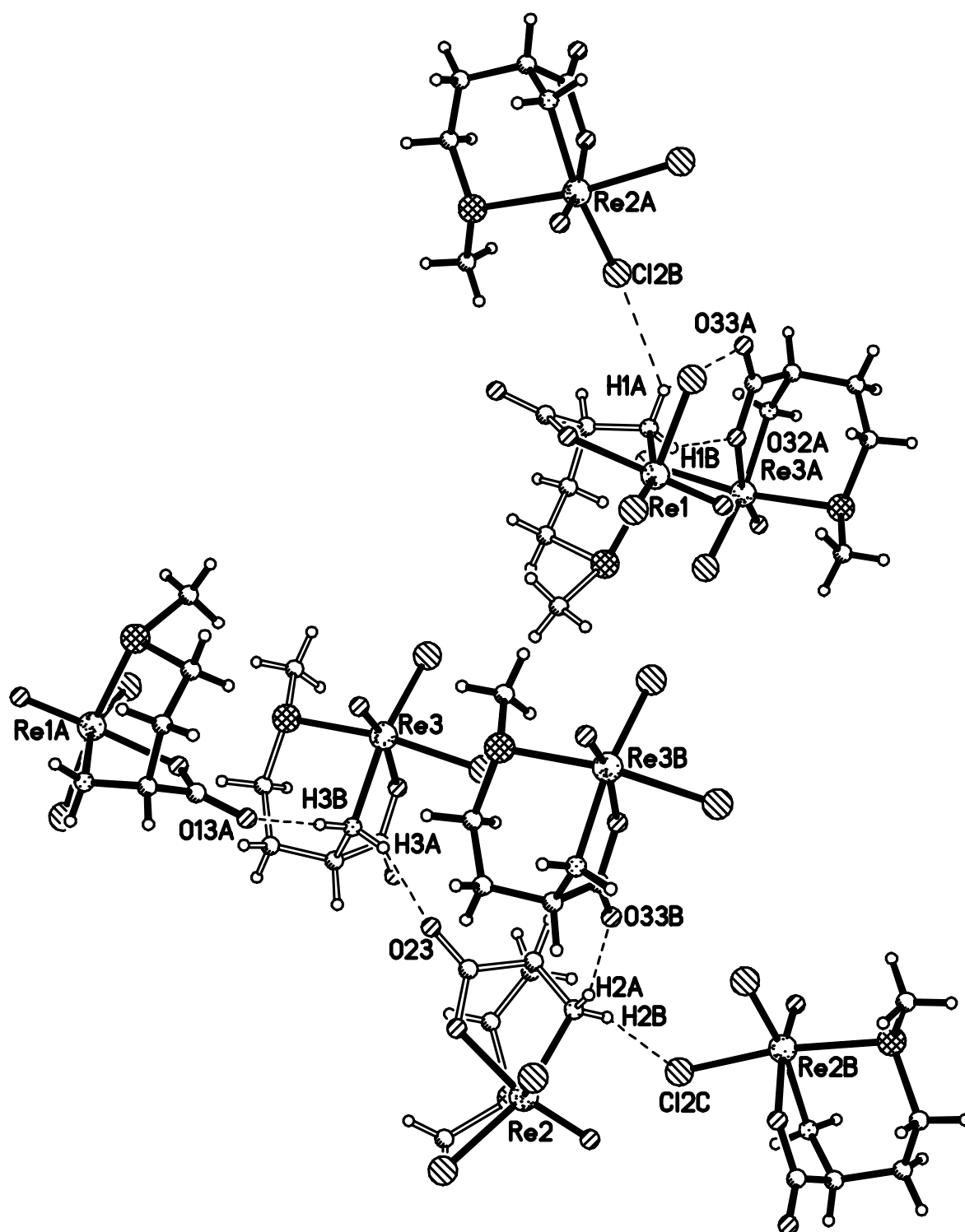


Figure S–1. Hydrogen-bonding pattern for crystal **1a**.

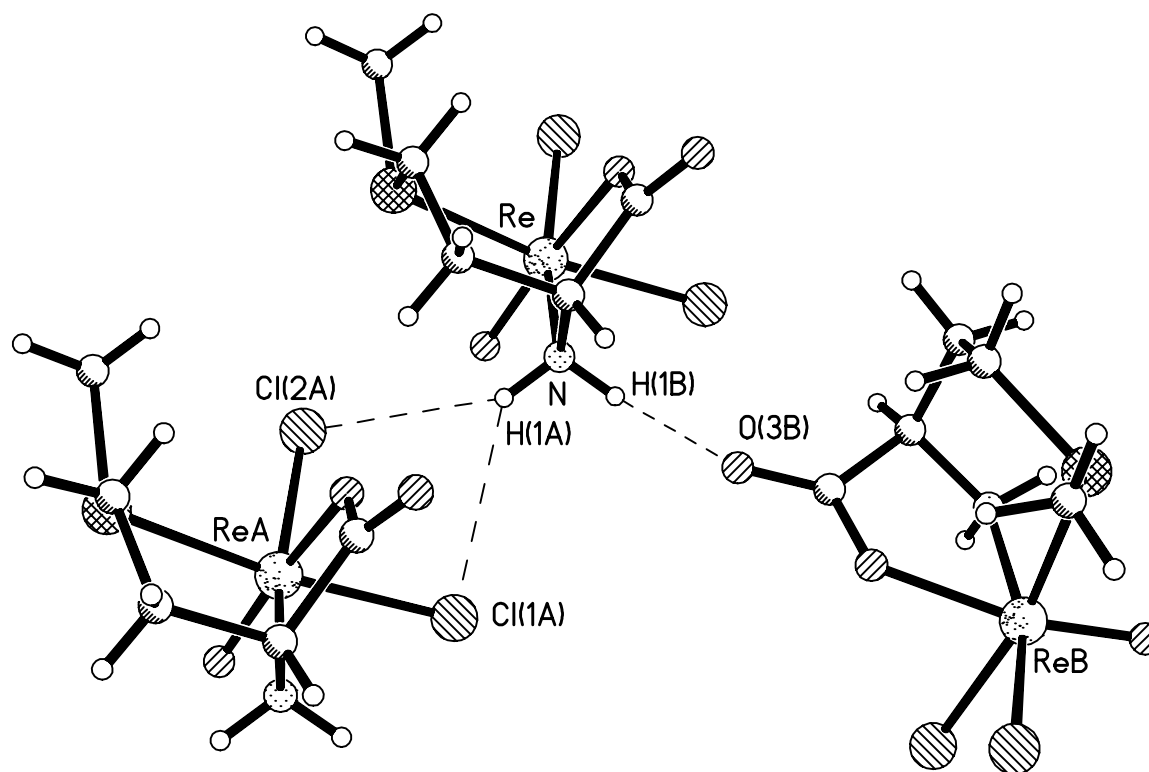


Figure S–2. Hydrogen-bonding pattern for crystal **2**.

The three independent molecules in compound **1a** (Fig. S-1) show different hydrogen-bonding patterns. In molecule 1, the amine proton H1A bonds to a carboxylate oxygen from a symmetry-related molecule 3 (3A) and a chloro ligand from a symmetry-related molecule 2 (2A), while H1B bonds to the other carboxylate oxygen from 3A. In the case of molecule 2, H2A also bonds to a carboxylate oxygen from 3B, while H2B is linked to the chloro ligand of another symmetry-related molecule 2 (2B). Finally, H3A and H3B (molecule 3) bond to carboxylate oxygens from molecule 2 and a symmetry equivalent of molecule 1, respectively.

The hydrogen-bonding pattern for complex **2** is less complicated (Fig. S-2). One of the amine hydrogens is shared between the two chloro ligands of a symmetry-equivalent molecule in the unit cell, while the other bonds to a carboxylate oxygen from another molecule.

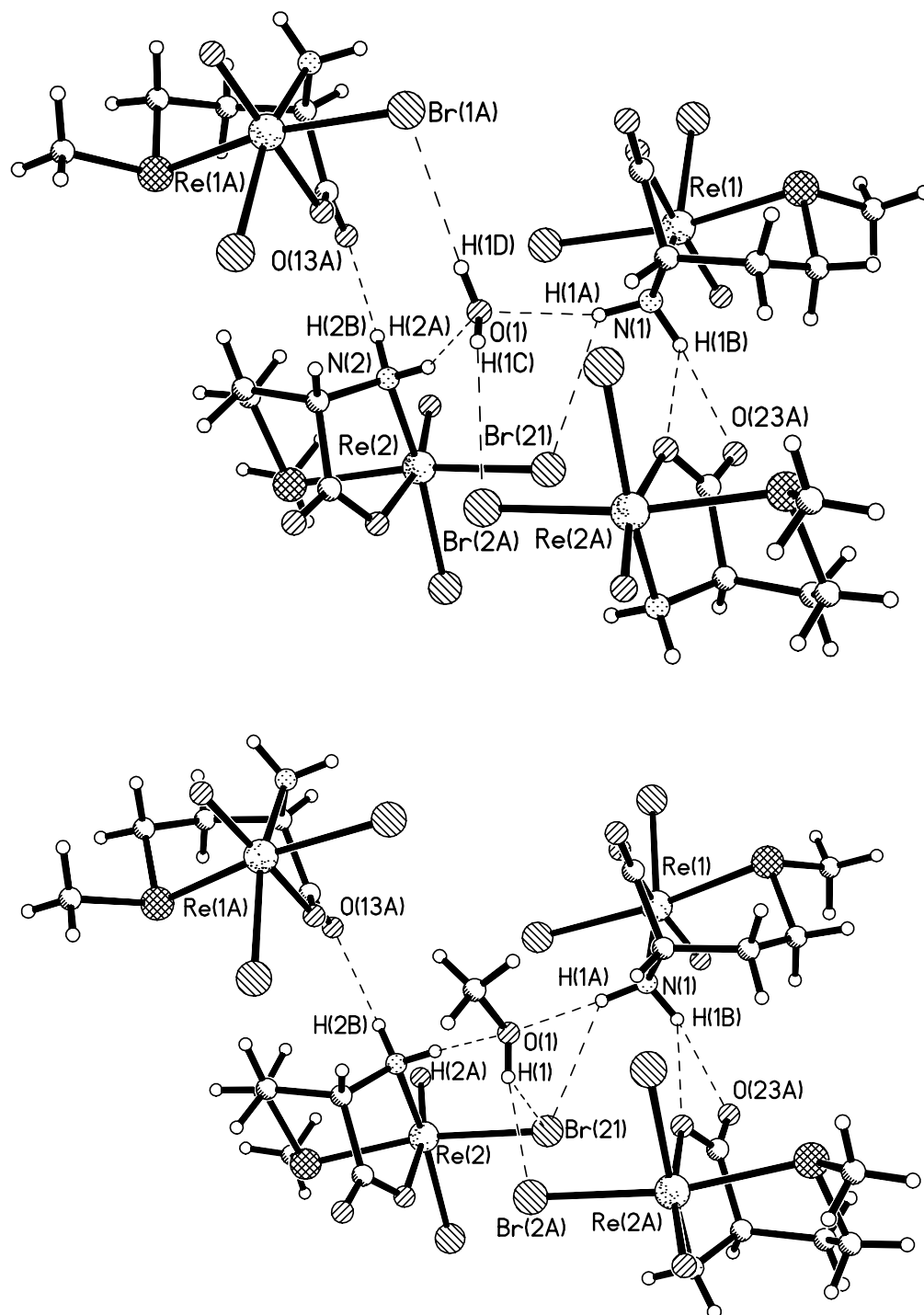


Figure S-3 Hydrogen-bonding pattern for crystals **3a** (top) and **3** (bottom).

The hydrogen-bonding pattern is similar for the two complexes. The oxygen atom from the solvent molecule (methanol or water) accepts one amine hydrogen from each molecule (H1A and H2A) and donates a hydrogen atom to a bromo ligand from a symmetry-related molecule (2A). In the case of **3a**, the other water hydrogen is bond to a bromo ligand provided by molecule 1A. The other amine hydrogen atoms (H1B and H2B) are bonded to the carboxylate ligands of molecules 2A and 1A, respectively.

Table S–6. Conformation of the Six–membered Rings in S,N,O- or S,N-coordinated Methionine Metal Complexes in the Literature.

Complex	Chirality	Comments ^b	Conformation	Coord.	Ref.
Ru(NO)(L–met)Cl ₂	S _S ,C _S S _R ,C _S	Disorder, 78% Disorder, 22%	Chair Boat	S,N,O	5
RuCl(D,L–met)(nbd) ^a	S _S ,C _S + S _R ,C _R S _S ,C _S + S _R ,C _R	Two ind. molec., centro	Chair	S,N,O	6
<i>trans</i> –S–[Co(L–met) ₂] ⁺	S _S ,C _S S _S ,C _S	Two met ligands on Co	Chair	S,N,O	7
<i>trans</i> –N–[Co(L–met) ₂] ⁺	S _S ,C _S S _S ,C _S	Two met ligands on Co	Chair	S,N,O	7
<i>trans</i> –O–[Co(L–met) ₂] ⁺	S _R ,C _S S _R ,C _S	Disorder Two met on Co	Boat/Chair (57/43) Chair	S,N,O	7
[Co(Cp*)(L–met)] ⁺	S _R ,C _S		Chair	S,N,O	8
Pt(D,L–metH)Cl ₂	S _S ,C _S + S _R ,C _R	Centro	Chair	N,S	9
Pt(L–metH)Cl ₂	S _R ,C _S S _S ,C _S	Two conf. in same unit cell	Chair	N,S	9,10
Pt(D–metH)Cl ₂	S _R ,C _R S _S ,C _R	Two conf. in same unit cell	Chair	N,S	11
Pt(L–metMe)Cl ₂	S _S ,C _S		Flattened chair	N,S	12
RuCl(L–metMe) ₂ (PPh ₃) ₂	S _R ,C _S S _R ,C _S	Two met ligands on Ru	Chair	N,S	13
RuCl(D,L–metMe)(nbd) ^a	S _R ,C _S + S _S ,C _R	Centro	Chair	N,S	6
Pd(D,L–met)Cl ₂	S _S ,C _S + S _R ,C _R	Centro	Flattened chair	N,S	14
Pd(L–met)Cl ₂	S _R ,C _S		Chair	N,S	15
Pd(D,L–metH)I ₂	S _S ,C _S + S _R ,C _R	Centro	Flattened chair	N,S	16
Pd(L–metMe)Cl ₂	S _R ,C _S		Chair	N,S	17
Pd(D,L–metMe)Cl(CH ₃)	S _R ,C _S		Chair	N,S	18
Pd(D,L–metMe)Cl(CH ₃ O)	S _R ,C _S + S _S ,C _R	Centro	Chair	N,S	18

^a nbd = norbornadiene; metMe = methionine methyl ester. ^b Space group is chiral unless otherwise indicated.

Detailed Signal Assignment for the Methionine Complexes

The spectra showed two signals at ~11 ppm and two more at 7.1-7.6 ppm which remained somewhat broader than the others, even at low temperature: they were assigned to N-H protons. On the basis of relative intensities, two sharp singlets between 2.7 and 3.0 ppm were attributed to the S-CH₃ protons. The rest of the spectra was rather complex, since C₂ is an asymmetric center, making the H_{3A}/H_{3B} and H_{4A}/H_{4B} protons nonequivalent. All signals in each set could be assigned from 2D spectra at -10°C, but the spectra were second-order and simulations were required. The strategy used to assign the C-H protons is described for the chloro complex. Since the lowest-field C-H signal of neutral and cationic methionine originates from H₂, the low-field signal at 4.789 ppm was assumed to be due to this same proton in one of the species, labeled Z. From a 2D COSY spectrum, the partner involved in its ³J coupling of 7.8 Hz was identified as the peak at 3.145 ppm, which then must arise from one of the H₃ protons. The other H₃ proton should also be coupled to H₂, but no cross peaks were detected in the 2D spectrum for the very small 1.1 Hz coupling eventually detected with the 2.537 ppm peak. At this point, the latter signal was assigned to the other H₃ proton on the basis of its large ²J coupling of 15.6 Hz to the 3.145 ppm peak. Cross-peaks of these two H₃ resonances with those at 4.643 and 3.672 ppm indicated that the latter pair must belong to the same species and correspond to H₄ protons. This assignment was supported by the large ²J constant of 12.7 Hz between the latter signals. Three of the vicinal coupling constants involving the H₃ and H₄ protons lied in the 3–6 Hz range, but the fourth one, between the signals at 2.537 and 3.672 ppm, was 12.2 Hz and had to correspond to a *trans* H–C–C–H arrangement. The other set of signals (Y) was assigned using the same procedure. Since the relative intensity of sets Y and Z is approximately 3:1, the stronger component for the S-CH₃ and each of the NH₂ protons could be assigned to Y.

Sets Y and Z had not yet been attributed to a particular isomer, and the H₃ and H₄ peaks had not been assigned individually. This was achieved by means of NOESY spectra. According to the structures found in the crystals, there is a short distance between an amine and an aliphatic proton in both isomers: this contact is between H_{3B} and H_{1B} for the *anti* isomer, but between H_{4A} and H_{1B} in the *syn* isomer (Fig. 1 and 2, respectively). Since a NOESY cross-peak is obtained between the signals at 2.676 and 7.42 ppm, respectively, the Y series must be assigned to the *anti* isomer, and the protons involved should be H_{3B} and H_{1B}, respectively. Likewise, the NOESY cross-peak between the 3.672 and the 7.20 ppm resonances in set Z are consistent with their assignment to H_{4A} and H_{1B} in the *syn* isomer.

Table S–7 Thermodynamic and Kinetic Data for the Inversion at the Coordinated S-CH₃ Group in **1a** (400 MHz).

Temperature (K)	Regime	Data	K (s ⁻¹)
233	Slow ^a	$h_e-h_o = 22.0$ Hz	69
245	Slow ^a	$h_e-h_o = 25.2$ Hz	79
258	Slow ^a	$h_e-h_o = 32.1$ Hz	101
271	Intermediate	$\Delta v_e = 56.4$ Hz	118
293	Intermediate	$\Delta v_e = 46.4$ Hz	138
297	Coalescence	$\Delta v_o = 77.6$ Hz	172

^a In slow exchange: $k = \pi(h_e-h_o)$, where h_e and h_o represent the full width at half-height.

^b In intermediate exchange: $k = \pi \cdot 2^{-1/2} \cdot (\Delta v_o^2 - \Delta v_e^2)^{1/2}$, where Δv_o and Δv_e are peak separations (in Hz) for spectra without and with exchange effects, respectively.

^c At the coalescence temperature: $k = \Delta v_o \cdot \pi / 2^{1/2}$.

Table S-8. IR Data and Tentative Assignments for the Ligands^a

His-Ala	His-Gly	His-Phe	His-Leu	
	3390s			$\nu_a(\text{NH}_3^+)$
	3343s			$\nu_a(\text{NH}_3^+)$
3209s	3247w	3190m	3213m	$\nu_s(\text{NH}_3^+)$
3143s	3136m	3146w	3145m	$\nu(\text{C-H})$ {Im, ν_3 }
3031vs	3070m	3063m	3080s	$\nu(\text{N-H})$ {peptide}
2981s			2957s	$\nu_a(\text{CH}_3)$
2955s	2965m	2950m	2957s	$\nu(\text{C}_\alpha\text{-H})$ {his}
	2937m	2930m	2941m	$\nu(\text{C}_\alpha\text{-H})$ {aa}
2911s			2870w	$\nu_s(\text{CH}_3)$
	2852m	2819m	2822m	$\nu_s(\text{CH}_2)$
1682vs	1660vs	1678vs	1680vs	$\nu(\text{C=O})$ {Amide I}
1635m	1625vs	1601sh	1617sh	$\delta_a(\text{NH}_3^+)$
1609m, sh	1583vs	1584vs	1587vs	$\nu_a(\text{COO}^-)$
1552vs, br	1551vs	1566vs 1540vs	1567vs 1538vs	$\delta(\text{N-H})$ {Amide II}
1502sh	1500s	1497w	1481m	$\nu(\text{C}_2=\text{N}_1) + \delta(\text{C}_2\text{-H})$ {Im, ν_8 }
		1480w		$\nu(\text{R})$ {phe}
1468m			1469m	$\delta_a(\text{CH}_3)$
1451m	1457w	1454w	1449m	$\delta(\text{CH}_2)$
	1440m	1441m		$\delta(\text{CH}_2)$
1431w	1428m	1430m	1432s	$\delta(\text{N-H}) + \nu(\text{C}_2\text{-N}_3)$ {Im, ν_{11} }
1394s	1390vs	1401s	1393vs	$\nu_s(\text{COO}^-)$
		1385w		$\delta(\text{C-H})$
1374m			1365m	$\delta_s(\text{CH}_3)$
1346m	1350w	1367w	1339m	$w(\text{CH}_2)$
1333m	1340w	1325w		$t(\text{CH}_2)$
1321w	1314m	1316m	1312m	Amide III, $\delta(\text{C-H})$ {aa}
1301s 1285m	1298m	1297w 1283w	1291w	$\delta(\text{CH}_2)$; $\delta(\text{C-H})$
1274m	1262s	1274m	1272m	$\nu(\text{C}_2=\text{N}_1)+\nu(\text{C}_5\text{-N}_1)+\nu(\text{C}_4\text{-N}_3)$ {Im, ν_{13} }
1247m	1243m	1256s	1255s	$\nu(\text{C}_4\text{-N}_3)+\nu(\text{C}_5\text{-C}_6)+\nu(\text{C}_5\text{-N}_1)$ {Im, ν_{14} }
1219s	1226m	1206w	1219w	$\delta(\text{C}_{2,4}\text{-H}) + \nu(\text{C}_4\text{-N}_3)$ {Im, ν_{15} }
		1193w		$\nu(\text{R})$ {phe}
		1176w		$\delta(\text{C-H})$ {R, phe}
		1165w		$\delta(\text{C-H})$ {R, phe}
1139s	1160m	1154m	1158m	$\nu(\text{C}_2\text{-N}_3) + \delta(\text{N-H})$ {Im, ν_{16} }
			1127w	Skel. $\{-\text{C}(\text{CH}_3)_2\}$
1113m	1115sh	1113s	1114s	$\nu(\text{C-N}) + \nu(\text{C-C})$ {aa}

Table S-8 (continued)

1084m	1099s	1101m	1103m 1094w	$\nu(\text{C}_4\text{--N}_3) + \delta(\text{C}_4\text{--H}) \{\text{Im}, \nu_{17}\}$
		1080w		$\delta(\text{C--H}) \{\text{R}, \text{phe}\}$
				$\nu(\text{C--O}) + \delta(\text{COH}) \{\text{ser}\}$
1056w	1026m	1048m	1057m	$\nu(\text{C--N}) + \nu(\text{C--C}) \{\text{aa}\}$
		1030w		$w(\text{C--H}) \{\text{R}, \text{phe}\}$
999w	1000m	1013m	1014m	$\nu(\text{C}_4=\text{C}_5) + \delta(\text{R}) \{\text{Im}, \nu_{19}\}$
961s	978w	966m	970m	$\delta(\text{R}) + \nu(\text{C}_5\text{--N}_1) \{\text{Im}, \nu_{20}\}$
937sh	939m	946s	947m	$\delta(\text{R}) \{\text{Im}, \nu_{21}\}$
928w			930w	$\rho(\text{CH}_3)$
901s	911w	910w	913w	$\rho(\text{CH}_2) +$
879 w	891w	894m	893m	$\nu(\text{C--C}) +$
	868s	839s	842s	$\nu(\text{C--N})$
847s	850m	854s	856vs	$\nu(\text{C--CO}_2^-)$
797s	810m	800m	806w	$w(\text{C--H}) + \gamma_t(\text{R}) \{\text{Im}, \nu_{22}\}$
		769w		$w(\text{C--H}) \{\text{R}, \text{phe}\}$
722w	738w 701w	744m	744s 726s	$\delta(\text{COO}^-)$
661w			686m	
		698vs		$\delta_{\text{oop}}(\text{R}) \{\text{phe}\}$
640s	672m	665s	666vs	$\delta(\text{R}) + \nu(\text{C--CH}_2) \{\text{Im}, \nu_{25}\}$
625s	627s	619w	618w	$\gamma_t(\text{R}) + w(\text{C--CH}_2) \{\text{Im}, \nu_{26}\}$
	589m		587m	$\delta(\text{N--C--C})$
		548m		$\delta(\text{R}) \{\text{phe}\}$
542m	572w	528w	533m	$\delta(\text{COO}^-)$
499m	480m	500m	471m	$\rho(\text{NH}_3^+)$

^a Notations in this and the following table : ν , stretching; δ , deformation (in-plane bending); w , wagging (out-of-plane bending); t , twisting; γ_t , torsion; oop , out-of-plane; ρ , rocking; R , aromatic ring
The ν_i labels used for the vibrations in the imidazole ring are as defined in Table 2 of the publication of Hasegawa, Ono and Noguchi.¹⁹

Tentative assignments in this and the following tables are proposed on the basis of comparisons with 4-methylimidazole,^{19,20} various amino acids²¹⁻²⁶ and dipeptides.^{27,28}

Table S-9. IR Data and Tentative Assignments for the Complexes^a

2	4	6	8	
3211s	3210s	3204s	3206s	$\nu_s(\text{NH}_2)$
3132s	3130s	3134s	3131s	$\nu(\text{C-H})$ {Im}
3033s	3033s	3030s	3033s	$\nu(\text{N-H})$ {peptide}
			2959s	$\nu(\text{CH}_3)$
2917s	2922s	2917s	2928s	$\nu(\text{C-H})$
1727s	1734s	1729s	1725s	$\nu(\text{C=O})$ (acid)
1633vvs	1642vvs	1632vvs	1634vvs	$\nu(\text{C=O})$ {Amide I}
1591s	1590s	1601sh	1592sh	$\delta(\text{NH}_2)$
1563s	1563s	1565s	1562s	$\delta(\text{N-H})$ {Amide II}
1495s	1495s	1496s	1497s	$\nu(\text{C}_2=\text{N}_1)+\nu(\text{C}_2-\text{N}_3)+\delta(\text{C}_2-\text{H})$ {Im, ν_8 }
1454m			1468m	$\delta_a(\text{CH}_3)$
		1454m		$\nu(\text{R})$ (phe)
1436m	1434m	1436m	1437m	$\delta(\text{N-H})+\nu(\text{C}_2-\text{N}_3)+\nu(\text{C}_4-\text{N}_1)$ {Im, ν_{11} }
	1416m			CH_2 scissor (gly)
1384m	1384s	1384m	1385m	$\delta(\text{OH})$
			1369w	$\delta_s(\text{CH}_3)$
1348w	1351w	1349w	1348w	$w(\text{CH}_2)$
1332w	1337w	1338w	1338w	$t(\text{CH}_2)$
1301m	1299m	1301w	1300w	$\nu(\text{C}_2=\text{N}_1)+\nu(\text{C}_5-\text{N}_1)+\delta(\text{C-H})$ {Im, ν_{13} }
1259s	1260s	1260s	1261s	$\nu(\text{C}_4-\text{N}_3)+\nu(\text{C}_5-\text{C}_6)+\nu(\text{C}_5-\text{N}_1)$ {Im, ν_{14} }
1222m	1222m	1222m	1229m	$\delta(\text{C}_{2,4}-\text{H}) + \nu(\text{C}_2=\text{N}_1)$ {Im, ν_{15} }
1193m	1194m	1197m	1192m	$\nu(\text{C-O})$ (acid)
1166s	1169m	1168s	1169s	$\nu(\text{C}_2-\text{N}_3)+\delta(\text{N-H})+\delta(\text{C}_2-\text{H})$ {Im, ν_{16} }
			1122m	Skel. ($-\text{C}(\text{CH}_3)_2$) {leu}
				$\nu(\text{C-O})$ {ser}
1084s	1085s	1084s	1084s	$\nu(\text{C}_4-\text{N}_3) + \delta(\text{C}_{2,4}-\text{H})$ {Im, ν_{17} }
1014vs 1000vs	1010vs	1015vs	1002vs	$\nu(\text{Re=O})$
922s	924m	921s	923m	$\delta(\text{O-H})$
905sh	906m	906sh	910sh	$\delta(\text{R})$ {Im, ν_{21} }
845m	824m	836m	838m	$w(\text{C}_{2,4}-\text{H}) + \gamma_t(\text{R})$ {Im, ν_{22} }
781m	779m	790w	796w	$\nu(\text{C-COOH})$
		748sh		$w(\text{C-H})$ {R, phe}
724m	724s	722sh	723s	$w(\text{C=O}) + \nu(\text{C-C})$
694m	694s	701vs	696s	$\delta_{\text{oop}}(\text{R})$ {phe} + $w(\text{COO})$
643w	643w	644w	644w	$\delta(\text{COO})$
620s	620s	620s	622s	$\gamma_t(\text{R}) + w(\text{N-H})$ {Im, ν_{27} }
592w	591w	600w	598w	$w(\text{O-H})$
		569w		$\delta(\text{R})$ {phe}
540s	540w	540m	542s	$w(\text{O-H})$
502m	496w	505w	503w	$\delta(\text{CCO})$

^a Notation as in Table S-8. The spectra of the chloro and bromo compounds are almost identical. The data for the bromo compounds are listed here.

Table S-10. Selected Bond Angles in **5a**.

	Molecule 1	Molecule 2	Litterature ^{a,b}
O=Re–O	166.4(3)	166.5(3)	164(2)
O=Re–N(Im)	95.3(4)	96.1(4)	91(2)
O–Re–N(Im)	79.2(3)	79.0(3)	81(3)
O=Re–NH ₂	95.1(3)	94.6(3)	91(1)
O–Re–NH ₂	72.3(3)	72.7(3)	74(1)
N(Im)–Re–NH ₂	86.7(4)	86.5(4)	89(1)
O=Re–Br2	105.8(3)	105.8(3)	106(1)
O–Re–Br2	86.8(2)	87.0(2)	89(1)
N(Im)–Re–Br2	90.5(3)	90.8(3)	90(2)
NH ₂ –Re–Br2	159.1(2)	159.6(2)	163(1)
O=Re–Br1	100.2(3)	99.4(3)	100(2)
O–Re–Br1	84.9(2)	85.1(2)	87(2)
N(Im)–Re–Br1	164.1(3)	164.0(3)	168(2)
NH ₂ –Re–Br1	88.4(2)	88.2(2)	88(1)
Br1–Re–Br2	88.66(5)	88.91(5)	89(2)
C8–O2–Re	117.5(7)	116.2(7)	121(1)
C2–N1–Re	122.7(9)	122.3(9)	126(1)
C5–N1–Re	128.0(9)	128.9(9)	127(1)
N2–C7–C8	104.4(9)	105.7(9)	109(1) ^c
C7–C8–O2	117.4(9)	119.1(9)	121(1) ^c
C7–C8–N4	121(1)	120(1)	115(1) ^c
O2–C8–N4	121(1)	120(1)	125(1) ^c

^a ReOX₂(his)₂ and ReOX₂(met). In the latter complexes, the angles involving N(Im) are replaced by those involving S. For the chloro compounds, the angles with Br are replaced by those involving Cl.

^b Mean value (standard deviation), 10 data.

^c In free His-aa dipeptides; 11 data. References given in Table S-4.

Table S-11A. Selected Torsion Angles^a for Compound **5a**.

	Molecule 1	Molecule 2
Ψ_1 (N2–C7–C8–N4)	157.5(10)	160.1(9)
ω (C7–C8–N4–C10)	167.6(9)	171.9(9)
ϕ_2 (C8–N4–C10–C11)	-52.8(2); -55.3(2)	-51.2(2); -55.7(2)
Ψ_2 (N4–C10–C11–O4')	-34(4); 149(4)	150(2); -38(3)
Ψ_2 (N4–C10–C11–O3')	149(4); -34(4)	-32(3); 144(3)
χ_1^{21} (C7–C6–C5–N1)	-14(2)	-19(2)
χ_1^1 (N2–C7–C6–C5)	60.3(12)	64.2(11)
C8–C7–C6–C5	-57.3(13)	-53.5(12)

^a Defined according to the IUPAC-IUB Commission on Biochemical Nomenclature²⁹

Most of the angles in the dipeptide (Table S-10) are not appreciably affected by coordination, except for N2–C7–C8 and C7–C8–O2, which decrease by 3–4° because of the strain imposed by the closure of five-membered ring. The reduction of C8–O2 bond order is also responsible for significant changes on the angles around C8: C7–C8–O2 (-3°), O2–C8–N4 (-4°) and C7–C8–N4 (+6°).

Selected torsion angle are listed in Table S-11A. The Ψ_1 angle describing the relative orientation of the peptide C=O bond and terminal C–NH₂ bond (C–NH₃⁺ in the free peptide) is ~159°, a value very close to those observed for free His-Ala (157°)³⁰ and other His-aa peptides (Table S-11B). The ω angle (~169°), which probes the planarity about the peptide link, is the same as in His-Ala, but this deviation of ~10° from the perfectly *trans* arrangement is greater than usually found in free His-aa dipeptides. Constraints imposed by chelate ring closure probably contribute to this distortion.

Dipeptide folding is described from the ϕ_2 and Ψ_2 torsion angles.^{31,32} The results in Table 7 are close to the idealized values of -60° and -30°, respectively, for a right-handed helical (folded) conformation.³³ Although this pattern is not obeyed in His-Ala itself,³⁰ alanine is believed to promote this conformational feature in proteins.³⁴ Conformational changes imposed by coordination are measured from the χ_1^{21} , χ_1^1 and C8–C7–C6–C5 torsion angles in the histidine residue. The values of 62° and -55° for the last two angles are correlated with the facial tridentate coordination leading to conformation **III** (Scheme 4), where the C6-imidazole bond is gauche with respect to both C7–C8 and C7–NH₂. The χ_1^{21} angle describes the relative orientation of the imidazole ring and peptide plane. Ideally, this angle should be ±90°, but a departure up to 32° is observed in the free dipeptides (Table S-11A). In the complexes, coordination imposes a more severe constraint (χ_1^{21} ca. -17°) to bring the imidazole ring close to coplanarity with the peptide plane.

Table S–11B. Torsion Angles in Dipeptides Containing N-terminal Histidine^a

	Ψ_1	ω	ϕ_2	Ψ_2	χ_1^1	χ_1^{21}	Ref.
His-Leu	164	175	-78	-19	65	69	32
His-Gly ^b	147	-178	130	180	-52	-58	35
His-Gly ^b	166	179	-78	-27	70	78	35
His-Ala	157	165	-110	74	-59	-83	30
His-Ser	128	174	-136	172	-71	78	31
His-Gly ^c	177	-164	-94	173	60	-94	36
His-Ala ^d	172	180	-55	-44	-87	-70	37
His-Ala ^d	169	175	-47	-52	-82	-70	37
His-Gly.HCl	146	174	175	177	-58	-79	38
His-Gly.2HCl	142	176	68	31	-59	93	39
His-Try.2HCl	142	175	-153	172	54	94	40

^a Defined according to the IUPAC-IUB Commission on Biochemical Nomenclature²⁹^b Two independent molecules in the asymmetric unit.^c In the L-Asp-L-Phe/L-His-Gly 1:1 complex.^d Complexes with oxalic acid.

Table S–12. Hydrogen-bonding Data for Complex **5a**.

	<i>D</i> –H (Å)	H··· <i>A</i> (Å)	<i>D</i> ··· <i>A</i> (Å)	<i>D</i> –H··· <i>A</i> (°)
N12–H12A···N4	0.90	2.17	2.94(1)	142.9
N12–H12B···Br2	0.90	2.48	3.373(9)	169.1
N13–H13···N5	0.86	2.13	2.87(2)	144.2
N14–H14A···Br2 ^a	0.86	2.43	3.288(8)	178.2
N22–H22A···N3	0.90	2.31	3.04(1)	138.2
N22–H22B···Br1 ^b	0.90	2.40	3.299(8)	176.8
N23–H23···O1 ^a	0.86	1.98	2.79(2)	157.3
N24–H24A···Br1 ^c	0.86	2.42	3.274(8)	169.6
O1–H1A···Br1	0.82(6)	2.59(4)	3.322(9)	149(8)
O1–H1B···Br2	0.81(5)	2.58(4)	3.339(10)	154(9)
O14'–H14'···O23'	0.82	1.85	2.66(2)	173.9
O24'–H24'···O13'	0.82	1.87	2.68(2)	172.2
O14''–H14''···O23''	0.82	1.89	2.70(2)	169.1
O24''–H24''···O13''	0.82	1.83	2.64(2)	172.7

^a x-1/2, -y+1/2, -z+2; ^b x, y+1, z; ^c x+1/2, -y+1/2, -z+2

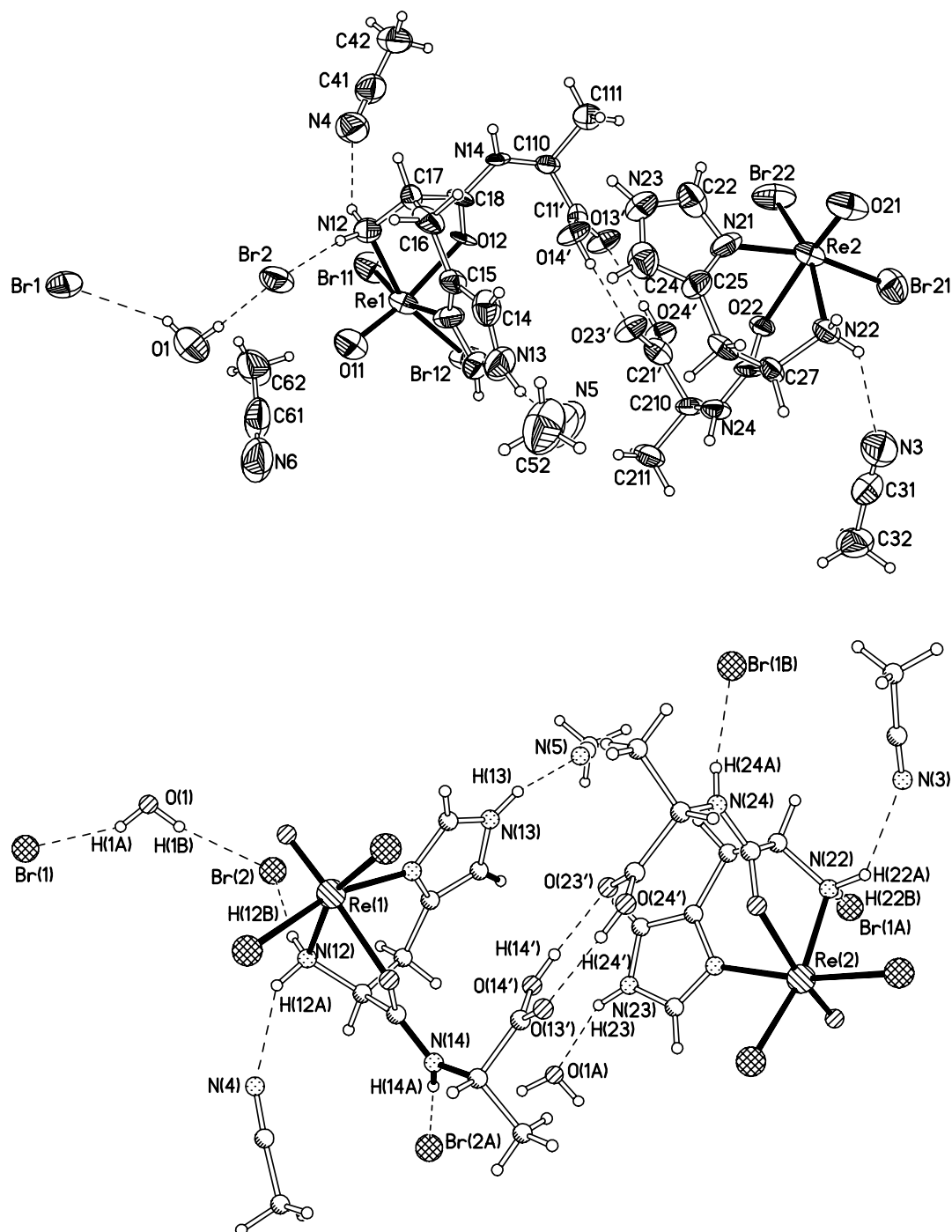


Figure S-4. Two views of hydrogen bonding in the asymmetric unit for **5a**.

In both cations, one NH_2 proton is hydrogen-bonded to a lattice acetonitrile molecule, while the other forms an $\text{N-H}\cdots\text{Br}^-$ bond with a counter-ion. The same counter-ion simultaneously acts as an acceptor for another $\text{N-H}\cdots\text{Br}^-$ bond involving the amide N-H proton. The imidazole H3 atom in molecule 1 acts as a donor to a lattice acetonitrile molecule, while the same proton in molecule 2 is linked to a water molecule. Finally, the water molecules are donors to two Br^- ions

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