not strictly statistically significant. Nevertheless, taken together these results are not inconsistent with the conclusion that there is more π back bonding from Co to C(C)O(C) than to the other carbonyl ligands. This point is one of several that we are currently addressing through extended Hückel molecular orbital calculations on $[(CO)_3CoB_{10}H_{12}]^-$ and related species.

Distances and angles within the $[PhCH_2NMe_3]^+$ cation are unexceptional and fully consistent with those determined in recent studies in this department (Mitchell & Welch, 1987; Wynd & Welch, 1989).

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Three Chromium(III) Complexes with Mixed Amino Acid Ligands: (L-Cysteinato)-(L-histidinato)chromium(III) 3·5-Hydrate, (L-Aspartato)(L-histidinato)chromium(III) 1·5-Hydrate and Bis(DL-histidinato)chromium(III) Chloride 4·2-Hydrate

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Abstract. [Cr(L-Cys)(L-His)].3·5H_2O (I): [$Cr(C_6H_8N_3O_2)(C_3H_5NO_2S)$].3·5$H_2O$, M_r = 388·4, orthorhombic, $P2_12_12_1$, a = 13·808 (2), b = 20·228 (3), c = 23·367 (5) Å, V = 6526·6 Å^3, Z = 16, D_x = 1·581 g cm^{-3}, Mo $K\alpha$, λ = 0·71069 Å, μ = 8·12 cm^{-1}, $F(000)$ = 3232, T = 294 K, final R = 0·037 for 4668 reflections. [Cr(L-Asp)(L-His)].1·5H_2O (II): [$Cr(C_4H_5NO_4)(C_6H_8N_3O_2)$].1·5$H_2O$, M_r = 364·2, orthorhombic, $P2_122_1$, a = 6·135 (1), b = 11·398 (1), c = 20·191 (1) Å, V = 1411·9 Å^3, Z = 4, D_x = 1·713 g cm^{-3}, Mo $K\alpha$, λ = 0·71069 Å, μ = 7·99 cm^{-1}, $F(000)$ = 752, T = 294 K, final R = 0·037 for 1253 observed reflections. [Cr(DL-His)$_2$]Cl.4·2H_2O (III): [$Cr(C_6H_8N_3O_2)_2$]Cl.4·2H_2O, M_r = 471·4, orthorhombic, $Ccca$, a = 15·334 (3), b = 32·038 (8), c = 16·635 (2) Å, V = 8172·3 Å^3, Z = 16, D_x = 1·532, Mo $K\alpha$, λ = 0·71069 Å, μ = 7·00 cm^{-1}, $F(000)$ = 3920, T = 294 K, final R = 0·056 for 1789 reflections. The ligands in all three complexes are tridentate. In (I) (four complexes per asymmetric unit) and (II) the arrangement of the ligands is *fac-cis*-N(amino), *cis*-O(carboxyl). In (III) two isomers, *fac-trans*-N(imidazole) and *fac-trans*-N(amino), cocrystallize. Metal–ligand bond lengths are: Cr—N(amino) 2·043 (5)–2·068 (5) Å, Cr—O(carboxyl) 1·963 (3)–1·998 (4) Å, Cr—S(thiol) 2·371 (2)–2·397 (2) Å, Cr—N(imidazole) 2·037 (4)–2·078 (5) Å. There is evidence that Cr—S(thiol) bonds exert a structural *trans* effect, and that their lengths in turn are influenced by the softness of the ligand in the *trans* position.

Introduction. Few structure analyses of amino acid complexes of Cr have been reported. Among these

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only one represents a complex with mixed amino acid ligands. We have determined the structures of the title compounds in order to produce additional benchmark values for the interactions of Cr with more complex biological ligands such as peptides and proteins.*

Experimental. [Cr(L-Cys)(L-His)].3·5H_2O: A solution of Cr^{III} nitrate nonahydrate (1·00 g, 2·5 mmol), L-cysteine (0·30 g, 2·5 mmol) and L-histidine (0·39 g, 2·5 mmol) in water (15 ml) was heated under reflux. Sodium hydroxide (0·30 g, 7·5 mmol) in water (10 ml) was added to the boiling solution. The mixture was refluxed for 3 h, then concentrated on a rotary evaporator at 313 K. The viscous solution was applied to a Sephadex A-25 anion exchange column and eluted with water. The second of three distinct bands was collected, then again concentrated at 313 K. Large well formed crystals were obtained after slow cooling of the hot solution. Structure solved by direct methods (Sheldrick, 1976), all non-H atoms anisotropic, H atoms included at sites calculated assuming idealized geometry (C—H, 0·97; N—H, 0·91 Å). Block-matrix least-squares refinement on F converged with shifts $<0·1\sigma$ in positional parameters of non-H atoms. Maximum excursions in a final difference map were 0·4 and $-0·3$ e Å^{-3}.

[Cr(L-Asp)(L-His)].1·5H_2O: Prepared as described by Watabe, Yano, Odaka & Kobayashi (1981). Structure solved by Patterson methods, all non-H atoms anisotropic, H atoms located and refined. Block-matrix least-squares refinement on F converged with all shifts $<0·5\sigma$. Maximum excursions in a final difference map were 0·4 and $-0·5$ e Å^{-3}.

[Cr(DL-His)$_2$]Cl.4·2H_2O: A solution of Cr^{III} chloride hexahydrate (2·66 g, 10 mmol), DL-histidine (1·88 g, 12 mmol) in water acidified with HCl (pH = 3·5) was heated for 30–40 min at 333 K. Saturated potassium hydroxide was added dropwise to the warmed solution until the pH reached 8. The purple precipitate which formed on cooling overnight was filtered off. Large orange crystals were observed in the solution after several weeks. Structure solved by Patterson methods, origin chosen at $\bar{1}$, non-H atoms refined anisotropically, H atoms included at calculated sites with isotropic temperature factors except for water H atoms which were refined with fixed bond lengths and angles. Full-matrix least-squares refinement on F converged with shifts $<0·1\sigma$. Maximum excursions in a final difference map were 0·5 and $-0·4$ e Å^{-3}.

All crystals mounted on glass fibres with epoxy resin, data collected using Enraf–Nonius CAD-4 automatic diffractometer, graphite-monochromated Mo $K\alpha$ radiation; 25 independent reflections with $19 \leq 2\theta \leq 25°$ used for least-squares determination of cell constants. Intensities of three reflections monitored, less than 3% decomposition in each case.

Calculations were performed using the *SHELX*76 system of programs (Sheldrick, 1976). Figures were drawn using *ORTEP* (Johnson, 1965). Scattering factors (neutral Cr for Cr^{III}) and anomalous-dispersion terms were taken from *International Tables for X-ray Crystallography* (1974). Data collection and refinement parameters are collected in Table 1. Final positional parameters are listed in Tables 2, 3 and 4.*

Table 1. *Summary of data collection and processing parameters for* [Cr(L-*Cys*)(L-*His*)].3·5H_2O (I), [Cr(L-*Asp*)(L-*His*)].1·5H_2O (II) *and* [Cr(DL-*His*)$_2$]Cl.-4·2H_2O (III)

	(I)	(I)	(III)
Crystal dimensions (mm)	0·10 × 0·18 × 0·18	0·40 × 0·09 × 0·10	0·15 × 0·15 × 0·25
Data collection range (°)	$2 < 2\theta < 50$	$2 < 2\theta < 50$	$2 < 2\theta < 50$
Scan width (°)	1·00 + 0·35tanθ	1·00 + 0·35tanθ	1·00 + 0·35tanθ
Horizontal counter aperture (°)	2·40 + 0·50tanθ	2·40 + 0·50tanθ	2·40 + 0·50tanθ
Scan type	ω–θ	ω–4θ/3	ω–θ
Absorption correction:*			
number of sampling points	6 × 6 × 6	6 × 6 × 6	8 × 8 × 8
maximum correction	1·15	1·11	1·11
minimum correction	1·07	1·06	1·09
Range of *hkl*	*h*: 0–16	*h*: 0–7	*h*: 0–18
	k: 0–23	*k*: 0–13	*k*: 0–36
	l: 0–27	*l*: 0–23	*l*: 0–19
Total data collected	6348	1486	4072
Data with $I > 2·5\sigma(I)$	4668	1253	1789
Total variables	816	265	288
R	0·037	0·037	0·056
wR	0·041	0·053	0·079
Weighting constant† k $\{w = 1/[\sigma^2(F_o) + kF_o^2]\}$	0·0035	0·0013	0·0039
GOF	1·64	—	—

* Coppens, Leiserowitz & Rabinovich (1965).
† Weighting constants refined, σ determined from counting statistics.

Discussion. The structures of the metal complexes are shown in Figs. 1–4. The asymmetric unit of (I) consists of four independent complexes each with a *cis*-N(amino),*cis*-O(carboxyl),*trans*-N(imidazole)/S(thiol) arrangement of the ligands, and 14 water molecules. In (II) there is only one independent complex, and 1·5 water molecules are disordered over three sites. The arrangement of the donor atoms in the complex is *cis*-N(amino),*cis*-O(carboxyl),*trans*-N(imidazole)/O(carboxyl). In (III) there are two independent complexes, one chloride is disordered

* Asp = $NH_2CH(CH_2COO^-)COO^-$, His = $NH_2CH(CH_2C_3N_2H_3)COO^-$, Cys = $NH_2CH(CH_2S^-)COO^-$, Pen = $NH_2CH[C(CH_3)_2S^-]COO^-$ (penicillamine).

* Structure amplitudes, anisotropic thermal parameters of non-H atoms, full lists of bond lengths and angles, positional and thermal parameters of H atoms, details of hydrogen bonds and close contacts, and results of least-squares-planes calculations have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 52414 (67 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Table 2. *Atomic coordinates and* B_{eq} (Å^2) *values with e.s.d.'s in parentheses for* [Cr(L-*Cys*)(L-*His*)].3·5H_2O

	x	y	z	B_{eq}*
Cr(1)	0·6177 (1)	0·6252 (1)	0·6555 (1)	2·12
S(11)	0·6739 (1)	0·6264 (1)	0·7514 (1)	2·93
O(11)	0·5049 (3)	0·6808 (2)	0·6773 (2)	2·56
O(12)	0·4161 (3)	0·6933 (2)	0·7570 (2)	2·90
N(11)	0·5229 (3)	0·5549 (2)	0·6852 (2)	2·43
C(11)	0·4852 (4)	0·5859 (3)	0·7382 (3)	2·47
C(12)	0·4652 (4)	0·6598 (3)	0·7239 (3)	2·40
C(13)	0·5682 (4)	0·5844 (3)	0·7813 (3)	2·81
O(13)	0·7029 (3)	0·6987 (2)	0·6320 (2)	2·93
O(14)	0·8180 (3)	0·7237 (2)	0·5693 (2)	4·15
N(12)	0·7349 (3)	0·5712 (2)	0·6278 (2)	2·55
N(13)	0·4766 (4)	0·6336 (3)	0·4963 (2)	3·03
N(14)	0·5685 (3)	0·6183 (2)	0·5717 (2)	2·39
C(14)	0·7811 (4)	0·6107 (3)	0·5820 (3)	3·05
C(15)	0·7691 (5)	0·6830 (3)	0·5948 (3)	3·20
C(16)	0·7308 (5)	0·5957 (3)	0·5243 (3)	3·07
C(17)	0·6256 (4)	0·6148 (3)	0·5223 (2)	2·41
C(18)	0·5683 (5)	0·6260 (3)	0·4763 (3)	2.77
C(19)	0·4800 (5)	0·6287 (3)	0·5527 (3)	2·98
Cr(2)	−0·0620 (1)	0·6346 (1)	0·1400 (1)	1·99
S(21)	−0·1075 (1)	0·5985 (1)	0·2332 (1)	2·68
O(21)	0·0539 (3)	0·5780 (2)	0·1417 (2)	2·55
O(22)	0·1751 (3)	0·5505 (2)	0·2007 (2)	3·86
N(21)	0·0320 (3)	0·6942 (2)	0·1854 (2)	2·57
C(21)	0·0804 (4)	0·6453 (3)	0·2231 (3)	2·09
C(22)	0·1088 (4)	0·5873 (3)	0·1860 (3)	3·08
C(23)	0·0058 (5)	0·6217 (3)	0·2680 (3)	3·45
O(23)	−0·1510 (3)	0·5718 (2)	0·1016 (2)	2·56
O(24)	−0·2861 (3)	0·5650 (3)	0·0516 (2)	3·86
N(22)	−0·1830 (3)	0·6933 (2)	0·1325 (2)	2·11
N(23)	0·0624 (4)	0·6857 (3)	−0·0176 (2)	3·28
N(24)	−0·0226 (3)	0·6701 (2)	0·0608 (2)	2·35
C(24)	−0·2334 (4)	0·6720 (3)	0·0800 (2)	2·31
C(25)	−0·2255 (4)	0·5973 (3)	0·0770 (2)	2·53
C(26)	−0·1896 (5)	0·7064 (3)	0·0270 (3)	2·80
C(27)	−0·0842 (4)	0·6927 (3)	0·0178 (3)	2·63
C(28)	−0·0309 (5)	0·7017 (3)	−0·0307 (3)	3·05
C(29)	0·0649 (5)	0·6667 (3)	0·0377 (3)	3·01
Cr(3)	0·6136 (1)	0·6916 (1)	0·2928 (1)	1·85
S(31)	0·6246 (1)	0·6299 (1)	0·2058 (1)	2·46
O(31)	0·4758 (3)	0·6626 (2)	0·3001 (2)	2·52
O(32)	0·3422 (3)	0·6560 (3)	0·2473 (2)	3·97
N(31)	0·5472 (3)	0·7602 (2)	0·2416 (2)	2·73
C(31)	0·4743 (4)	0·7197 (3)	0·2112 (3)	2·79
C(32)	0·4250 (4)	0·6764 (3)	0·2560 (3)	2·70
C(33)	0·5269 (5)	0·6751 (3)	0·1697 (3)	3·12
O(33)	0·6794 (3)	0·6226 (2)	0·3385 (2)	1·99
O(34)	0·8104 (3)	0·6038 (2)	0·3921 (2)	3·29
N(32)	0·7536 (3)	0·7257 (2)	0·2876 (2)	2·43
N(33)	0·5365 (4)	0·7948 (3)	0·4413 (3)	3·91
N(34)	0·6024 (3)	0·7485 (2)	0·3659 (2)	2·49
C(34)	0·8005 (4)	0·7075 (3)	0·3427 (3)	2·47
C(35)	0·7631 (4)	0·6389 (3)	0·3598 (2)	2·28
C(36)	0·7796 (4)	0·7590 (3)	0·3886 (3)	2·99
C(37)	0·6753 (5)	0·7681 (3)	0·4032 (3)	3·03
C(38)	0·6334 (6)	0·7969 (3)	0·4487 (3)	3·86
C(39)	0·5199 (5)	0·7653 (3)	0·3909 (3)	3·20
Cr(4)	0·4652 (1)	−0·0639 (1)	0·1957 (1)	1·72
S(41)	0·4310 (1)	−0·0989 (2)	0·2916 (1)	2·34
O(41)	0·5968 (3)	−0·1029 (2)	0·2024 (2)	2·32
O(42)	0·7077 (3)	−0·1169 (2)	0·2711 (2)	3·69
N(41)	0·5380 (4)	0·0115 (2)	0·2372 (2)	2·58
C(41)	0·5958 (4)	−0·0255 (3)	0·2794 (3)	2·61
C(42)	0·6402 (4)	−0·0858 (3)	0·2505 (3)	2·30
C(43)	0·5265 (5)	−0·0509 (3)	0·3255 (3)	2·95
O(43)	0·4004 (3)	−0·1424 (2)	0·1628 (2)	2·23
O(44)	0·2713 (3)	−0·1749 (2)	0·1132 (2)	2·87
N(42)	0·3305 (3)	−0·0242 (2)	0·1828 (2)	2·06
N(43)	0·5820 (4)	−0·0204 (3)	0·0351 (2)	2·97
N(44)	0·4990 (3)	−0·0321 (2)	0·1140 (2)	2·29
C(44)	0·2900 (4)	−0·0603 (3)	0·1328 (2)	2·22
C(45)	0·3203 (4)	−0·1319 (3)	0·1362 (2)	2·05
C(46)	0·3279 (5)	−0·0303 (3)	0·0764 (3)	2·65
C(47)	0·4354 (4)	−0·0315 (3)	0·0688 (2)	2·11
C(48)	0·4867 (5)	−0·0249 (3)	0·0189 (3)	2·80
C(49)	0·5881 (5)	−0·0249 (3)	0·0924 (3)	3·04
OW(1)	−0·1931 (4)	−0·0613 (3)	−0·6369 (2)	3·85
OW(2)	−0·0299 (4)	−0·3602 (3)	−0·5434 (3)	5·40
OW(3)	−0·1172 (4)	−0·1633 (3)	−0·8671 (2)	4·13
OW(4)	−0·3183 (4)	−0·1777 (3)	−0·8843 (2)	3·99
OW(5)	−0·2494 (4)	−0·1928 (3)	−0·1419 (2)	4·44
OW(6)	−0·2518 (4)	0·0026 (3)	−0·0329 (2)	4·71
OW(7)	−0·4284 (6)	−0·0224 (4)	−0·4776 (4)	7·85
OW(8)	−0·4321 (5)	−0·3287 (4)	−0·0825 (3)	6·58
OW(9)	−0·1860 (6)	−0·1434 (3)	−0·4300 (4)	8·22
OW(10)	0·4735 (5)	0·0933 (4)	0·4845 (3)	7·09
OW(11)	−0·3878 (6)	−0·1781 (4)	−0·3843 (4)	9·11
OW(12)	−0·2279 (6)	−0·0657 (5)	−0·3261 (4)	9·70
OW(13)	−0·1450 (8)	−0·0212 (4)	−0·8687 (4)	10·71
OW(14)	−0·1680 (7)	−0·1214 (5)	−0·0522 (5)	11·81

* $B_{eq} = (8\pi^2/3)(U_{11} + U_{22} + U_{33})$.

Table 3. *Atomic coordinates and* B_{eq} (Å^2) *with e.s.d.'s in parentheses for* [Cr(L-*Asp*)(L-His)].1·5H_2O

	x	y	z	B_{eq}*
Cr(1)	0·1038 (1)	0·2007 (1)	0·1226 (1)	3·07
O(2)	0·3822 (6)	0·1589 (3)	0·1652 (2)	3·77
O(3)	0·2048 (6)	0·1244 (4)	0·0410 (2)	3·69
N(4)	0·0206 (7)	0·0367 (4)	0·1546 (2)	3·18
O(5)	0·5752 (5)	0·0057 (4)	0·1996 (2)	4·18
O(6)	0·2517 (6)	−0·0196 (4)	−0·0316 (2)	4·67
C(7)	0·2235 (8)	−0·0315 (5)	0·1510 (2)	3·09
C(8)	0·4117 (8)	0·0479 (5)	0·1745 (2)	3·16
C(9)	0·2623 (8)	−0·0741 (6)	0·0808 (2)	3·59
C(10)	0·2365 (7)	0·0151 (5)	0·0265 (2)	3·43
O(11)	0·1785 (7)	0·3549 (4)	0·0856 (2)	5·00
N(12)	−0·1954 (8)	0·2454 (4)	0·0854 (2)	3·59
O(13)	0·0400 (12)	0·5349 (4)	0·0774 (2)	7·37
N(14)	−0·0003 (8)	0·2801 (4)	0·2084 (2)	4·08
N(15)	−0·0346 (12)	0·3191 (4)	0·3135 (2)	5·66
C(16)	−0·2089 (12)	0·3759 (5)	0·0915 (3)	4·76
C(17)	0·0193 (13)	0·4269 (5)	0·0841 (2)	5·24
C(18)	−0·3029 (12)	0·4045 (6)	0·1604 (3)	5·23
C(19)	−0·1730 (11)	0·3573 (5)	0·2165 (3)	4·47
C(20)	−0·1921 (14)	0·3813 (6)	0·2820 (3)	5·84
C(21)	0·0816 (13)	0·2607 (5)	0·2683 (3)	4·72
O(22)†	−0·3113 (19)	0·7072 (9)	0·0627 (6)	7·69
O(23)†	−0·1846 (25)	0·7543 (12)	0·0949 (7)	7·28
O(24)†	−0·5716 (23)	0·6114 (12)	0·0540 (6)	9·24

* $B_{eq} = (8\pi^2/3)(U_{11} + U_{22} + U_{33})$.
† Occupancies: O(22) 0·64, O(23) 0·50(2), O(24) 0·64(1).

over two sites separated by 2·17 Å, and 4·2 water molecules are disordered over seven sites. The ligands at the two independent Cr atoms are arranged differently: one Cr has the *cis*-N(amino),-*cis*-O(carboxyl),*trans*-N(imidazole) arrangement observed previously in [Cr(L-His)$_2$]NO_3.H_2O (Pennington, Cordes, Kyle & Wilson, 1984), and the other has a *trans*-N(amino),*cis*-O(carboxyl),*trans*-N(imidazole) arrangement. Both complexes lie on C_2 axes. It follows that the species occurring in the unit cell are [Cr(L-His)$_2$]$^+$ and [Cr(D-His)$_2$]$^+$. Curiously, when the analogous Co^{III} complex is prepared in a similar way, only the [Co(D-His)(L-His)]$^+$ species is observed (Bagger, Gibson & Sorensen, 1972; Thorup, 1977).

When α-amino acids act as tridentate ligands in an octahedral complex they are geometrically constrained to facial (*fac*) coordination. In the present series there are potentially three structural isomers of each complex, depending on the relative orientations of the two ligands. The potential isomers, and those which actually occur in the crystals, are as follows:

Complex	NH_2/NH_2	COO^-/COO^-	N_{imid}/X
(I), (II), (III)	*cis*	*cis*	*trans*
	cis	*trans*	*cis*
(III)	*trans*	*cis*	*cis*

Table 4. *Atomic coordinates and B_{eq} values* (Å^2) *with e.s.d.'s in parentheses for* [Cr(D,L-*His*)$_2$]Cl.4·2H$_2$O

Space group *Ccca*, origin at $\bar{1}$.

	x	*y*	*z*	B_{eq}*
Cr(1)	0·0000	0·3794 (1)	0·2500	3·93
Cr(2)	0·2500	0·5000	0·4528 (1)	3·38
O(1)	0·0838 (3)	0·4228 (1)	0·2816 (3)	4·33
O(2)	0·2152 (4)	0·4487 (2)	0·2532 (3)	5·31
O(3)	0·3459 (3)	0·4911 (1)	0·5294 (3)	3·92
O(4)	0·4707 (3)	0·4570 (2)	0·5454 (3)	5·03
N(1)	0·0673 (4)	0·3845 (2)	0·1432 (3)	4·06
N(2)	0·0891 (4)	0·3347 (2)	0·2799 (3)	4·66
N(3)	0·1530 (5)	0·2833 (2)	0·3417 (4)	6·44
N(4)	0·3505 (4)	0·4901 (2)	0·3737 (3)	4·28
N(5)	0·2298 (3)	0·4372 (2)	0·4537 (3)	3·73
N(6)	0·1733 (5)	0·3764 (2)	0·4826 (4)	5·44
C(1)	0·1566 (5)	0·3967 (2)	0·1661 (4)	4·63
C(2)	0·1536 (5)	0·4260 (2)	0·2381 (4)	4·33
C(3)	0·2114 (6)	0·3578 (2)	0·1864 (5)	5·54
C(4)	0·1736 (5)	0·3317 (2)	0·2520 (5)	5·06
C(5)	0·0800 (6)	0·3046 (2)	0·3337 (5)	5·65
C(6)	0·2128 (7)	0·2996 (2)	0·2906 (5)	6·11
C(7)	0·4094 (4)	0·4603 (2)	0·4130 (4)	4·48
C(8)	0·4119 (4)	0·4701 (2)	0·5034 (4)	3·85
C(9)	0·3785 (4)	0·4165 (2)	0·4005 (5)	4·86
C(10)	0·2909 (5)	0·4066 (2)	0·4358 (4)	4·30
C(11)	0·1607 (5)	0·4179 (2)	0·4810 (5)	4·92
C(12)	0·2565 (6)	0·3688 (2)	0·4543 (5)	5·48
Cl(1)†	0·1071 (2)	0·2058 (1)	0·4606 (2)	6·82
Cl(2)†	0·0039 (11)	0·1719 (6)	0·5213 (10)	9·59
O*W*(1)	0·3664 (6)	0·4576 (3)	0·1722 (5)	8·48
O*W*(2)†	0·0539 (8)	0·3262 (4)	0·5604 (6)	9·77
O*W*(3)†	0·4387 (9)	0·3787 (5)	0·1876 (8)	8·47
O*W*(4)	0·1491 (17)	0·2651 (7)	0·6110 (16)	30·32
O*W*(5)	0·4228 (51)	0·2500	0·2500	35·37
O*W*(6)†	0·5000	0·4910 (19)	0·2500	29·85
O*W*(7)†	0·5000	0·4230 (17)	0·2500	17·37

* $B_{eq} = (8\pi^2/3)(U_{11} + U_{22} + U_{33})$.

† Disordered atoms, occupancies: Cl(1) 0·80, Cl(2) 0·20, O*W*(2) 0·80, O*W*(3) 0·60, O*W*(6) 0·60, O*W*(7) 0·40.

Among the seven mononuclear 2:1 amino acid:Cr^{III} complexes which have been studied previously (Table 6), five have the *cis*-N(amino),*cis*-O(carboxyl) arrangement. The two exceptions are complexes where a *cis*-N(amino),*cis*-O(carboxyl) arrangement is prevented by steric interactions between bulky substituents on the N(amino) atoms (Mootz & Wunderlich, 1980*a*,*c*). In the present study, further examples of the *cis*-N(amino),*cis*-O(carboxyl) arrangement are found in (I), (II) and one isomer of (III). The second isomer of (III) is *trans*-N(amino),*cis*-O(carboxyl) and provides the first apparent exception to the general trend observed in other crystal structures. There are, however, precedents which suggest that the identification of one isomer or another in the crystalline state does not exclude the formation of other isomers. For example, [Cr(L-His)(L- or D-Cys)] isomerizes in water at temperatures above 278 K (Odaka, Hasegawa & Watabe, 1985); and the preparation of [Cr(L-His)$_2$]$^+$ yields two of the possible three isomers, one being identified as the *cis*-N(amino),*trans*-O(carboxyl) isomer on spectroscopic grounds (Hoggard, 1981), and the other as the *cis*-N(amino),*cis*-O(carboxyl) isomer by structure analysis (Pennington, Cordes, Kyle & Wilson, 1984). Thus it is probable that the relative preparative yields of [bis(amino acidato)Cr^{III}] isomers in the solid state are influenced not only by intramolecular steric and electronic effects but also by efficient packing and intermolecular hydrogen bonding (*i.e.* by solubility and crystallizability). The influence of intermolecular forces on the crystal structures of amino acidato complexes of kinetically labile metals such as Co^{II}, Ni^{II} and Zn^{II}

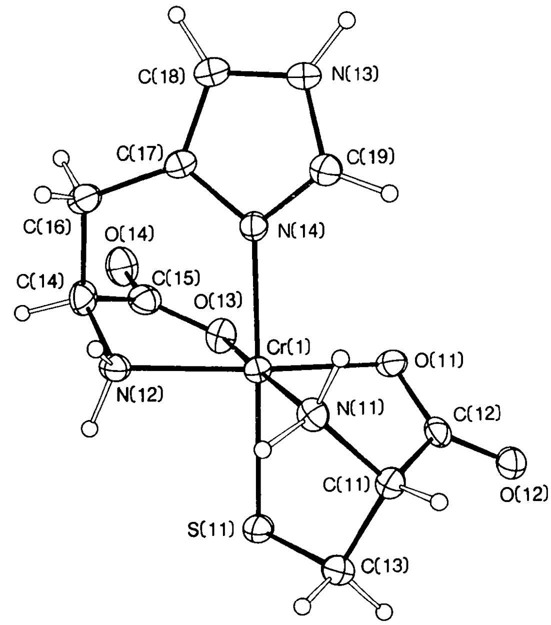

Fig. 1. View of [Cr(L-Cys)(L-His)] in compound (I).

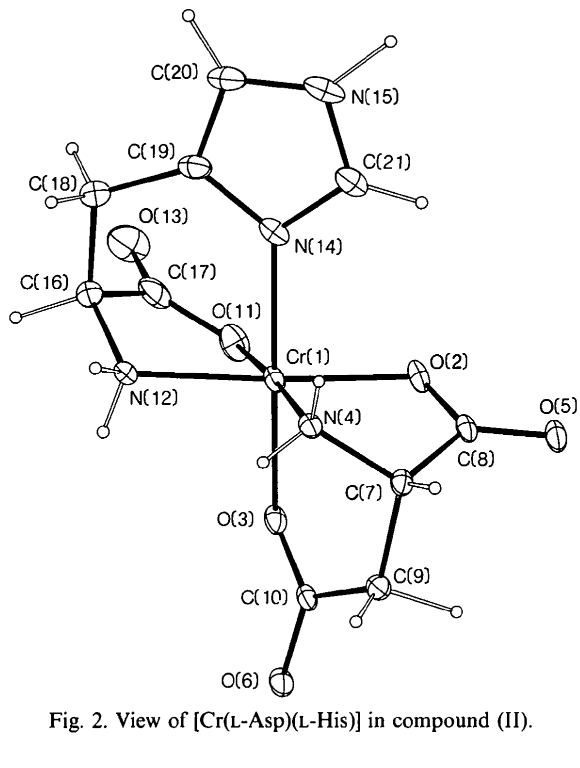

Fig. 2. View of [Cr(L-Asp)(L-His)] in compound (II).

has long been taken for granted (Freeman, 1967). On the time scale of the formation of crystals or solid precipitates, the relative kinetic inertness of Cr^{III} complexes becomes irrelevant.

The crystals of (I), (II) and (III) all contain extensive hydrogen-bond networks connecting N(amino) and O(water) atoms to Cl^-, S(thiol), O(carboxyl) and O(water) atoms. Compound (III) is noteworthy (Fig. 5). The structure consists of layers of complexes with their Cr atoms at $y = 0, \frac{1}{2}$ and near $y = 0 \pm \frac{1}{8}, \frac{1}{2} \pm \frac{1}{8}$, layers of water molecules and chloride ions near $y = \frac{1}{4}$, and channels of water molecules parallel to x near $y = 0, \frac{1}{2}$ at $z = \frac{1}{4}$. The Cr—N(amino), Cr—O(carboxyl) and – with one exception – Cr—N(imidazole) bond lengths found in the present study (Table 5) are within the ranges reported previously (Table 6). The longest Cr—N(imidazole) bond, 2·078 (5) Å, occurs in (I). We shall refer to it in our discussion of the Cr—S(thiol) *trans* effect (see below). The imidazole rings in all complexes are planar within 0·010 (3) Å.* The deviations of the Cr atoms from the imidazole ring planes are 0·23 (1)–0·48 (1) Å in (I), 0·13 (1) Å in (II), and 0·13 (1) Å [*trans* to N(amino)] and 0·24 (1) Å [*trans* to N(imidazole)] in (III). Similar deviations have been found in other octahedral Cr complexes of histidine (Pennington, Cordes, Kyle & Wilson, 1984). The range of values found in the four independent formula units of (I) suggests that the deviations of the Cr atoms are affected not only by intramolecular strain but also by crystal packing forces.

The lengths of the four independent Cr—S(thiol) bonds in (I), 2·371 (2)–2·397 (2) Å, span a range of 7σ (Table 5). The significant differences among these bond lengths may be caused partly by hydrogen bonding. The shortest Cr—S(thiol) bond in (I) is formed by S(11), which is involved in only one weak hydrogen bond; the other three S atoms are each involved in two relatively strong hydrogen bonds.

* See deposition footnote.

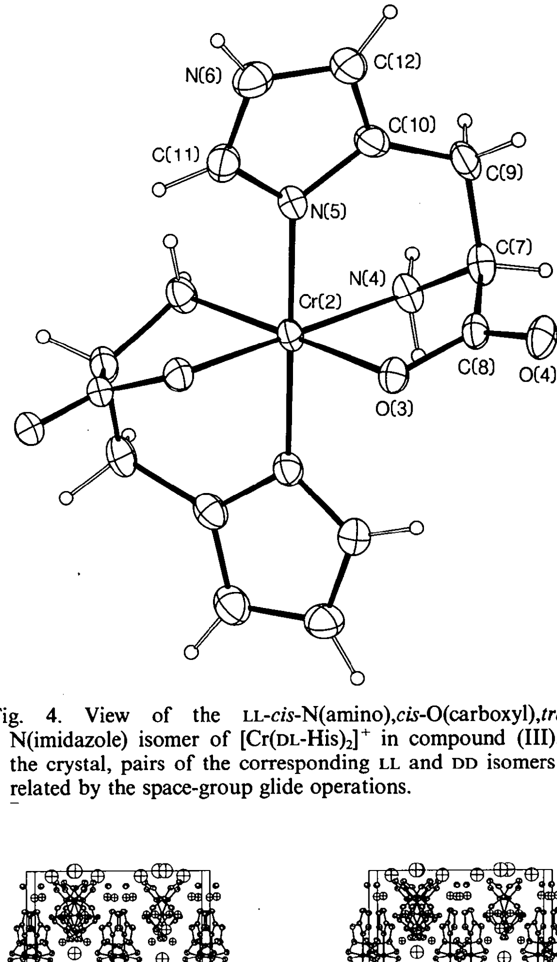

Fig. 4. View of the LL-*cis*-N(amino),*cis*-O(carboxyl),*trans*-N(imidazole) isomer of $[Cr(DL\text{-}His)_2]^+$ in compound (III). In the crystal, pairs of the corresponding LL and DD isomers are related by the space-group glide operations.

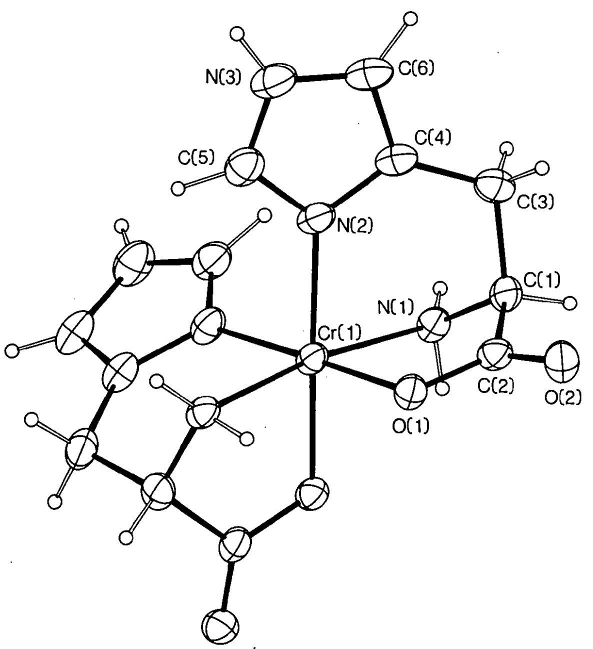

Fig. 3. View of the LL-*trans*-N(amino),*cis*-O(carboxyl),*cis*-N(imidazole) isomer of $[Cr(DL\text{-}His)_2]^+$ in compound (III). In the crystal, pairs of the corresponding LL and DD isomers are related by the space-group glide operations.

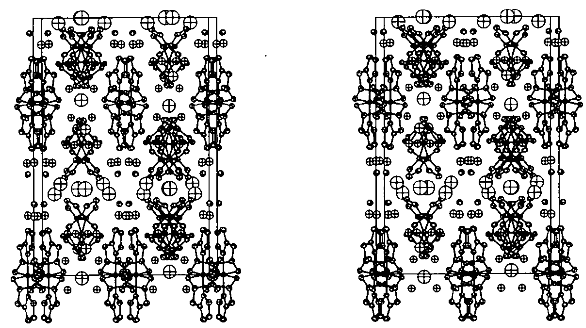

Fig. 5. Stereoview of the unit cell of [Cr(DL-His)$_2$]Cl.$4{\cdot}2H_2O$. Origin at bottom left ($0 \leq x \leq a$ into paper, $0 \leq y \leq 0{\cdot}75b$ vertical, $0 \leq z \leq c$ horizontal). (Unconnected spheres represent, in increasing order of size, Cl^- ions, ordered H_2O molecules and disordered H_2O molecules.)

Table 5. *Selected bond lengths* (Å) *and angles* (°) *in* [Cr(L-*Cys*)(L-*His*)].3·5H_2O [(I), *four formula units* 1–4], [Cr(L-*Asp*)(L-*His*)].1·5H_2O (II) *and* [Cr(DL-*His*)$_2$]Cl.4·2H_2O [(III), *two formula units* 1–2]

Compound / Complex	(I) 1	2	3	4	(II)	(III) 1*	2†
Cysteine/aspartate ligand							
Cr—N(amino)	2·053 (5)	2·065 (5)	2·048 (5)	2·068 (5)	2·043 (5)		
Cr—O(carboxyl)‡	1·988 (4)	1·968 (4)	1·998 (4)	1·987 (4)	1·970 (4)		
Cr—S(thiol)	2·371 (2)	2·380 (2)	2·389 (2)	2·397 (2)			
Cr—O(carboxyl)§					1·963 (3)		
N(amino)—Cr—O(carboxyl)‡	78·7 (2)	79·5 (2)	79·8 (2)	79·1 (2)	81·8 (2)		
N(amino)—Cr—S(thiol)	84·1 (1)	82·8 (1)	83·4 (1)	82·9 (1)			
N(amino)—Cr—O(carboxyl)§					86·5 (2)		
O(carboxyl)‡—Cr—S(thiol)	90·5 (1)	91·1 (1)	88·9 (1)	89·4 (1)			
O(carboxyl)‡—Cr—O(carboxyl)§					89·2 (1)		
Histidine ligand							
Cr—N(amino)	2·056 (5)	2·057 (5)	2·056 (5)	2·048 (5)	2·048 (5)	2·061 (5)	2·052 (5)
Cr—O(carboxyl)‡	1·974 (4)	1·983 (4)	1·978 (4)	1·978 (4)	1·964 (5)	1·064 (5)	1·967 (4)
Cr—N(imidazole)	2·078 (5)	2·059 (5)	2·067 (5)	2·068 (5)	2·057 (4)	2·041 (6)	2·037 (5)
N(amino)—Cr—O(carboxyl)‡	81·0 (2)	80·1 (2)	80·6 (2)	81·2 (2)	81·2 (2)	81·2 (2)	80·3 (2)
N(amino)—Cr—N(imidazole)	85·7 (2)	86·4 (2)	86·1 (2)	87·0 (2)	85·5 (2)	86·0 (2)	88·0 (2)
O(carboxyl)‡—Cr—N(imidazole)	89·0 (2)	88·8 (2)	88·9 (2)	89·5 (2)	89·9 (2)	89·6 (2)	88·1 (2)

* *trans*-N(Amino),*cis*-O(carboxyl),*cis*-N(imidazole) isomer.
† *cis*-N(Amino),*cis*-O(carboxyl),*trans*-N(imidazole) isomer.
‡ O atom of main-chain carboxyl group of L-Asp.
§ O atom of side-chain carboxyl group of L-Asp.

Table 6. Cr—N(*amino*), Cr—O(*carboxyl*) *and* Cr—N(*imidazole*) *distances* (Å) *in previously reported bis*(*α-amino acidato*)*chromium*(III) *complexes*

Complex	Cr—ligand distances: N(amino)	O(carboxyl)	N(imidazole)	S(thiol)	Reference
Na[Cr(L-Cys)$_2$].2H_2O	2·062 (2)	1·981 (1)		2·416 (1)	(*a*)
[Cr(L-His)(D-Pen)].H_2O	2·063 (4)	2·013 (4)	2·057 (5)		(*b*)
	2·094 (5)	1·989 (4)		2·332 (2)	
K[Cr{HN(CH_2COO)$_2$}$_2$].3H_2O	2·070 (6)	1·958 (4)			(*c*)
		1·969 (4)			
	2·058 (6)	1·958 (4)			
		1·954 (4)			
Na[Cr{*i*-C_3H_7N(CH_2COO)$_2$}$_2$].2H_2O	2·118 (2)	1·956 (2)			(*d*)
		1·972 (2)			
K[Cr{*t*-C_4H_9N(CH_2COO)$_2$}$_2$].4H_2O	2·152 (3)	1·953 (2)			(*e*)
		1·974 (2)			
[Cr(Ac-L-Ala)(L-His)].H_2O	2·062 (4)	1·957 (4)	2·036 (5)		(*f*)
	2·078 (5)	1·947 (4)			
		1·960 (3)			
[Cr(L-His)$_2$]NO_3.H_2O	2·043 (3)	1·972 (3)	2·062 (3)		(*g*)
	2·052 (4)	1·970 (3)	2·050 (3)		

References: (*a*) Meester, Hodgson, Freeman & Moore (1977); (*b*) Meester & Hodgson (1977*a*); (*c*) Mootz & Wunderlich (1980*b*); (*d*) Mootz & Wunderlich (1980*c*); (*e*) Mootz & Wunderlich (1980*a*); (*f*) Sato, Kosaka & Watabe (1985); (*g*) Pennington, Cordes, Kyle & Wilson (1984).
Abbreviations: *i*-$C_3H_7N(CH_2COO^-)_2$ = isopropyliminodiacetate; *t*-$C_4H_9N(CH_2COO^-)_2$ = *N-tert*-butyliminodiacetate; Ac-L-Ala = $(CH_2COO^-)NH-CH(CH_3)COO^-$, *N*-carboxylatomethyl-L-alaninate.

We conclude that Cr—S(thiol) bonds are weakened by hydrogen bonding at the S atom. The absence of a similar effect on Cr—N(amino) and Cr(carboxyl) interactions is possibly associated with the lower polarizabilities of the N and O donor atoms.

Evidence for a Cr—S(*thiol*) *trans effect.* Apart from the possible dependence of Cr—S(thiol) bond lengths on hydrogen bonding (see above), the values of the four independent Cr—S(thiol) bond lengths in (I) lead to a second correlation. Each of the four bonds is *trans* to an N(imidazole), and each is longer than the distance 2·332 (2) Å observed in [Cr(D-Pen)(L-His)].H_2O where the S(thiol) is *trans* to the O(carboxyl) of histidine (Meester & Hodgson, 1977*a*). An even longer Cr—S(thiol) distance, 2·416 (1) Å, occurs in Na[Cr(L-Cys)$_2$].2H_2O. In the latter complex, two S(thiol) atoms are *trans* to each other (Meester, Hodgson, Freeman & Moore, 1977). Thus it appears that the order of increasing Cr—S(thiol) bond length is also the order of increasing softness of the ligand atom *trans* to the S(thiol) atom [O < N(imidazole) < S]. Further, among the four independent Cr—S(thiol) bonds in (I), the shortest is *trans* to the longest Cr—N(imidazole) bond (the outlier to which we have referred above). This observation suggests a complementarity between the strengths of a Cr—S(thiol) bond and the bond *trans* to it.

The elongation of Cr—S bonds when they are *trans* to another S donor atom has been noted previously (Stein *et al.*, 1976; Meester, Hodgson, Freeman & Moore, 1977). Evidence for a lengthening of other Cr—ligand bonds *trans* to Cr—S(thiol) bonds in Cr^{III} complexes has previously been only marginal. In $[Cr(en)_2(S—CH_2COO^-)]^+$ the Cr—N bond *trans* to the Cr—S bond is 0·02 Å (1·5σ) longer than the mean of three Cr—N bonds *cis* to the Cr—S bond; in the analogous Co^{III} complex the difference is 0·04 Å (Elder, Florian, Lake & Yacynych, 1973). A case which appears to have escaped notice until now occurs in [Cr(L-His)(D-Pen].H_2O where the Cr—O(carboxyl) bond *trans* to the Cr—S(thiol) bond is significantly longer than all the other Cr—O(carboxyl) bonds of histidine ligands listed in Tables 5 and 6 (Meester & Hodgson, 1977*a*). The present work provides the first example of the lengthening of a Cr—N(imidazole) bond when it is *trans* to a strong Cr—S(thiol) bond. A possible explanation is that Cr—S(thiol) bonds cause, and are affected by, a ground-state *trans* effect (Stein *et al.*, 1976).

Such a structural *trans* effect would be consistent with kinetic evidence for a dynamic *trans* effect in Cr^{III}—S(thiol) complexes. For example, the coordinated S atom of $[(H_2O)_5CrSR]^{3+}$ and $[(H_2O)_5CrSH]^{2+}$ labilizes the *trans* site towards substitution by a variety of ligands. The Cr—S bond is, in turn, labilized by the incorporation of a ligand into the *trans* site, so that the substitution kinetics of $[(H_2O)_5CrSR]^{3+}$ reflect both the labilization of the H_2O *trans* to the Cr—S bond and the relative ease of Cr—S bond fission (Asher & Deutsch, 1976). The dynamic *trans* effect involves both the ground and excited states, whereas the structural *trans* effect is a ground-state phenomenon. The two effects must be connected but their origins are not yet clear.

According to a purely electrostatic theory, the structural *trans* effect can be described as a polarization of the thiolate ligand by the charge on the metal atom, the polarization of the metal atom by the induced dipole on the thiolate, and a resultant weakening of the bond to the ligand in the *trans* position (see for example Cotton & Wilkinson, 1980). The fact that Cr^{III}—S bonds are more labile than Co^{III}—S bonds in some reactions is then explained partly by the smaller crystal-field activation energy of the d^3 electron configuration (Weschler & Deutsch, 1973). The electrostatic model has some attraction since it accounts, at least qualitatively, for the observed Cr—S(thiol) bond length variations in response to the *trans* donor type and hydrogen-bonding effects.

On the other hand, recent evidence that imidazole (Winter, Caruso & Shepherd, 1988) and even Cl^- (Hambley & Lay, 1986) can act as π donors to Cr^{III} suggests that p_π–d_π interactions between the S and Cr atoms may also play a role. If the *trans* ligand competes with the S atom as a π donor, then the Cr—S(thiol) bond length should increase as the π donor effectiveness of the *trans* ligand increases, *i.e.* in the order O(carboxylate) (weak) < N(imidazole) (moderate) < S(thiol) (strong π donor). This is the case. The effect of hydrogen bonding at the S atom may be to reduce the contribution of the S p_z orbital to p_π–d_π bonding. An apparent weakness of this π bonding hypothesis is that it requires a vacancy in an orbital of suitable symmetry on the metal atom. Such a vacancy exists in the t_{2g}^3 configuration of Cr^{III} but not in the t_{2g}^6 configuration of Co^{III}. The structural *trans* effect of S(thiol) is, however, even greater in Co^{III} than in Cr^{III} complexes, as shown by the structure analyses of $[M(en)_2(S—CH_2COO^-)]^+$ (Elder, Florian, Lake & Yacynych, 1973) and [*M*(L-His)(D-Pen)].H_2O (Meester & Hodgson, 1977*a*,*b*). Accordingly, while π bonding may make a contribution, it is difficult to rationalize the *trans* effect of Cr—S(thiol) bonds in terms of π bonding alone.

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Structure of Bis(dimethylglyoximato-*N,N'*)(thiourea-*S*)copper(II)

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Abstract. Bis(2,3-butanedione dioximato-*N,N'*)(thiourea-*S*)copper(II), $[Cu(C_4H_7N_2O_2)_2(CH_4N_2S)]$, $M_r = 369\cdot88$, monoclinic, $P2_1/c$, $a = 15\cdot117$ (14), $b = 11\cdot569$ (6), $c = 8\cdot882$ (4) Å, $\beta = 103\cdot73$ (6)°, $V = 1508\cdot9$ (1·7) Å^3, $Z = 4$, $D_m = 1\cdot63$, $D_x = 1\cdot63$ g cm^{-3}, λ(Cu $K\alpha$) = 1·5418 Å, $\mu = 35\cdot261$ cm^{-1}, $F(000) = 764$, $T = 293$ K, $R = 0\cdot055$ for 1306 observed reflections. The coordination polyhedron around Cu^{II} is a distorted tetragonal pyramid with four N atoms of the dioximato ligands forming the basal plane [Cu—N distances in the range 1·946 (3)–1·956 (3) Å] and thiourea S-bonded at the apex [Cu—S 2·484 (1) Å].

Introduction. In our investigation of factors determining the stabilizing influence of dioximato ligands on Cu^{II} relative to Cu^{I}, several dioximato copper(II) complexes with reductive ligands, *e.g.* thiourea and its derivatives, triphenylphosphine and triphenylarsine, have been prepared. In order to clarify the bonding of the reductive ligands in these complexes, the crystal structure determination of the title complex was undertaken.

Experimental. Dark brown prismatic crystals, 0·30 × 0·40 × 0·20 mm; D_m measured by flotation: Weissenberg photographs indicated space group $P2_1/c$, Syntex $P2_1$ diffractometer; cell parameters by least squares from 15 reflections with $9\cdot69 \leq 2\theta \leq 31\cdot02°$; intensity measurements from θ–2θ scans carried out for $0 \leq 2\theta \leq 100°$; range of *hkl*: h $-17 \rightarrow 17$, k $0 \rightarrow 13$, l $0 \rightarrow 10$. Two standard reflections after every 98 intensity measurements, no significant intensity variation; no correction for absorption; 2030 unique reflections; 1306 independent reflections with $I \geq 3\sigma(I)$; Cu position from Patterson function, other non-H atoms from difference syntheses. Methyl and thiourea H atoms in calculated positions, oxime H atoms from difference syntheses. Anisotropic full-matrix refinement (except H atoms) based on *F*. $R = 0\cdot055$, $wR = 0\cdot060$, $w = k/[\sigma^2(F_o) + g(F_o)^2]$, $k = 1\cdot0763$ and $g = 0\cdot003101$; $(\Delta/\sigma)_{max}$ in final least-squares cycle 0·30; max. and min. heights in final difference Fourier synthesis = 0·8 and −0·4 e Å^{-3}. Calculations performed with *SHELX76* (Sheldrick, 1976); scattering factors from *International Tables for X-ray Crystallography* (1974).

Discussion. Atomic coordinates of non-H atoms are given in Table 1; selected interatomic distances and bond angles are listed in Table 2.† The crystal structure consists of neutral square-pyramidal $Cu(Hdmg)_2(tu)$ molecules with dioximato (Hdmg) ligands N-bonded in the equatorial plane and thiourea (tu) S-bonded in the apical position (Fig. 1).

The mean Cu—N distance [1·952 (4) Å] and the bond lengths and angles within the dioximato ligands agree well with those found in other five-coordinate complexes $Cu_2(Hdmg)_4$ (Vaciago & Zambonelli, 1970), $Cu(Hdmg)_2(im)$ (im = imidazole) (Morehouse, Polychronopoulou & Williams, 1980) and $Cu(Hdpg)_2(H_2O)$ (Hdpg = diphenylglyoxime) (Boualam & Gleizes, 1983).

The O—H···O hydrogen bonds appear to be asymmetric with both H atoms bonded to the same

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† Lists of structure factors, anisotropic thermal parameters and H-atom parameters have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 52401 (11 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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