Discussion. Table 1* contains final atomic positional parameters for the non-H atoms. Selected distances and angles are reported in Table 2. The molecular structure is presented in Fig. 1 (Johnson, 1976). The crystal structure consists of two symmetrically independent tetrameric modules in the unit cell, each of symmetry C_i^1 {the inversion centres are at (000) and $(\frac{1}{2}\frac{1}{2}\frac{1}{2})$ respectively for molecule 1 [U(1), U(2)] and molecule 2 [U(3), U(4)]}. In the tetrameric molecules, each U atom is seven coordinated in a distorted pentagonal-bipyramidal geometry. The pentagonal base of the bipyramid is defined by five O atoms which belong to four distinct acetate ligands assuming bridging between neighbouring U atoms (Fig. 1). Two of the bridging acetate groups are monodentate simultaneously towards two neighbouring U atoms. The other two acetate groups bridge by sharing one O between two U atoms, being monodentate with respect to one U and bidentate with respect to its neighbour. The bridging between the U atoms also occurs through one oxide O atom occupying the common apex of two adjacent bipyramids. The cyclopentadienyl ligands, one for each U, lie on the non-bridged apical coordination sites of the bipyramids. As expected, the cyclopentadienyl ligands are pentahapto bonded to the U atoms. The averaged U—C distance is 2.78 (2) Å. Corresponding U—O bond distances, in two tetrameric molecules, are in quite good agreement with an average value of 2.36 (1) Å for O atoms bonded to only one U in a monodentate mode (eight such), of 2.49 (1) Å for O atoms bonded to only one U in a bidentate mode (four such) and of 2.45 (1) and 2.581 (1) Å for bridging O atoms (four such) bonded simultaneously to two neighbouring U atoms in a monodentate mode and in a bidentate mode of bonding, respectively. There are no intermolecular distances shorter than normal van der Waals contacts.

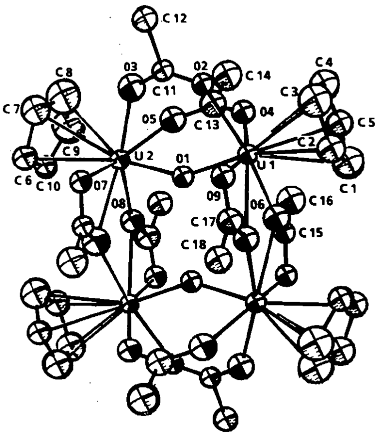

Fig. 1. The molecular structure. Thermal ellipsoids are at the 50% probability level.

References

Enraf–Nonius (1986). *Structure Determination Package*. Version 18. Enraf–Nonius, Delft, The Netherlands.

Johnson, C. K. (1976). *ORTEP*II. Report ORNL-5138. Oak Ridge National Laboratory, Tennessee, USA.

Walker, N. & Stuart D. (1983). *Acta Cryst.* A**39**, 158–166.

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* Lists of structure amplitudes, anisotropic thermal parameters and a complete list of bond lengths and angles have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 54592 (35 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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Structures of Zinc(II) with Tetradentate N_2S_2 Ligation

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Abstract. *trans*-3,3′-(1,2-Cyclohexanediyldinitrilo)-bis(2-methylpropane-2-thiolato)]zinc(II), $[Zn(C_{14}H_{28}N_2S_2)]$, Zn(2), $M_r = 353.89$, monoclinic, $C2/c$, $a = 17.914\ (4)$, $b = 9.440\ (1)$, $c = 10.877\ (2)$ Å, $\beta = 110.19\ (2)°$, $V = 1726\ (1)$ Å^3, $Z = 4$, $D_m = 1.35\ (1)$, $D_x = 1.360$ Mg m^{-3}, μ(Mo $K\alpha$, $\lambda = 0.71073$ Å) = 0.17 mm^{-1}, $F(000) = 752$, $T = 298\ (1)$ K, $R_F = 0.026$, $wR_F = 0.037$ for 1290 reflections. 3,3′-(1,2-Cyclohexa-1,4-dienediyldinitrilo)bis(2-methylpropane-2-thiolato)]zinc(II), $[Zn(C_{14}H_{24}N_2S_2)]$, Zn(3), $M_r = 349.86$, monoclinic, $P2_1/c$, $a = 9.760\ (2)$, $b = 17.326\ (3)$, $c = 10.530\ (2)$ Å, $\beta = 91.49\ (2)°$, $V =$

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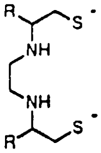
1780 (1) Å^3, $Z = 4$, $D_m = 1.31$ (1), $D_x = 1.305$ Mg m^{-3}, μ(Mo $K\alpha$, $\lambda = 0.71073$ Å) = 0.16 mm^{-1}, $F(000) = 736$, $T = 297$ (1) K, $R_F = 0.050$, $wR_F = 0.062$ for 1723 reflections. The structures consist of discrete complexes with distorted-tetrahedral ZnS_2(thiolate)N_2(amine) coordination geometries. Zn—S [2.2533 (6) Å for Zn(2); 2.259 (1), 2.253 (1) Å for Zn(3)] and Zn—N [2.101 (2) Å for Zn(2); 2.088 (4), 2.128 (4) Å for Zn(3)] distances are close to those reported for similar structures with bidentate N(amine)S(thiolate) ligands. The N,S chelate rings in both structures exhibit the envelope conformation with the tetrasubstituted C atoms comprising the flaps. In Zn(3), the central N,N chelate ring adopts the envelope conformation, while in Zn(2), the corresponding ring is *gauche*. The cyclohexane ring in Zn(2) shows the expected chair conformation, while the cyclohexa-1,4-diene ring in Zn(3) is planar to ±0.07 Å.

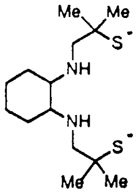
Introduction. We have been interested in low molecular weight Cu^{II} complexes having approximately tetrahedral N(imidazole)$_2$S(thiolate)$_2$ ligand sets. Such complexes would be useful spectroscopic models of blue Cu^{II} protein sites (Solomon, Penfield & Wilcox, 1983) and possibly the Cu(*A*) site in cytochrome *c* oxidase (Martin, Scholes & Chan, 1988). The redox instability of Cu^{II}-thiolate may be circumvented by using tetradentate N_2S_2 ligands such as (1) (Bharadwaj, Potenza & Schugar, 1986) or (2) (Bharadwaj, Fikar, Potenza, Zhang, Potenza & Schugar, 1992). These first generation models lack both the imidazole ligation and pseudotetrahedral geometry of the protein binding sites. A Cu(imidazole)$_4^{2+}$ complex with a pseudotetrahedral coordination geometry has recently been obtained using a novel bidentate ligand (Knapp, Keenan, Zhang, Fikar, Potenza & Schugar, 1990). To distort the approximately planar *cis*-N_2S_2 geometry of Cu^{II}(2) towards tetrahedral, we attempted to prepare Zn^{II}(2) and dope it with Cu^{II}. We report here the structures of the Zn^{II} complex of (2) and of an unexpected minor product (3), a dehydrogenated analogue of (2).



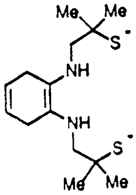
(1)

(1*a*) R = COOH

(1*b*) R = $COOCH_3$



(2)



(3)

Experimental. Zn^{II}(2) was prepared by displacement of tren [$N(CH_2CH_2NH_2)_3$] with the diprotonated form of (2). A deoxygenated solution of Zn(tren).2ClO$_4$ (0.215 g) and H$_2$-(2) (0.20 g) in 8 ml H$_2$O/acetonitrile (30/70 *v*/*v*) gave colorless crystals of Zn(2). A deoxygenated solution of Zn(tren).2ClO$_4$ (0.200 g), Cu(tren).2ClO$_4$ (0.015 g), and H$_2$-(2) (0.200 g) in 16 ml of H$_2$O/acetonitrile (50/50 *v*/*v*) yielded a few pale-purple crystals of Zn^{II}(3) before crystals of the major phase, colorless Zn^{II}(2), precipitated.

Structure solution: values for Zn(3) are given in parentheses. D_m by flotation; colorless prism 0.12 × 0.15 × 0.45 mm for Zn(2); pale-purple prism 0.11 × 0.17 × 0.40 mm for Zn(3); Enraf–Nonius CAD-4 diffractometer; graphite-monochromated Mo $K\alpha$ radiation; θ–2θ scan. Reciprocal-lattice symmetry and systematic absences consistent with monoclinic space groups *C*2/*c* and *Cc*(*P*2$_1$/*c*); *C*2/*c* by successful solution of Zn(2). Cell constants from setting angles of 25 reflections with $15.18 \le \theta \le 20.47°$ ($6.25 \le \theta \le 18.04°$); data corrected for Lorentz, polarization and absorption [empirical correction, ψ scan; transmission coefficient range 0.97–1.00 (0.82–1.00)] effects. Variation in intensity of three standard reflections ±0.5% (±1.2%); 1513 (2304) unique reflections measured with $4 \le 2\theta \le 50°$ ($4 \le 2\theta \le 45°$); 226 (89) reflections averaged, $R_F = 0.04$ (0.01); 1290 (1723) with $I \ge 3\sigma(I)$ used in refinement. Data collected: h 0, 21 (0, 10); k 0, 11 (0, 18); l −12, 12 (−11, 11). Structures solved by direct methods (*MULTAN*82; Main, Fiske, Hull, Lessinger, Germain, Declercq & Woolfson, 1982) and difference Fourier techniques; H atoms from difference Fourier maps and at calculated positions; C—H and N—H distances 0.95 and 0.87 Å; H atoms not refined. Full-matrix refinement on F; all atoms anisotropic; $w = 4F_o^2/[\sigma^2(F_o^2) + 0.0016F_o^4]$. Final $R_F = 0.026$ (0.050), $wR_F = 0.037$ (0.062), $S = 1.37$ (2.03), $\Delta\rho_{\max} = 0.24$ (0.63) e Å^{-3}, $(\Delta/\sigma)_{\max} = 0.01$ (0.01); 87 (172) variables. Scattering factors from *International Tables for X-ray Crystallography* (1974, Vol. IV). Programs from Enraf–Nonius (1983) *SDP*.

Discussion. Final positional parameters and their e.s.d.'s are given in Table 1.* Views of Zn(2) and of Zn(3), showing the atom-numbering schemes, are given in Fig. 1.

The structures consist of discrete Zn(2) or Zn(3) molecules with no intermolecular contacts shorter than those arising from van der Waals contacts. In

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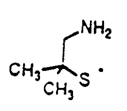
* Lists of structure factors, H-atom parameters, bond lengths and angles, and anisotropic thermal parameters have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 54676 (38 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Table 1. *Fractional atomic coordinates and isotropic thermal parameters* (Å²)

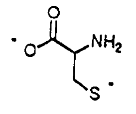
$$B_{eq} = (4/3)[a^2B(1,1) + b^2B(2,2) + c^2B(3,3) + ab(\cos\gamma)B(1,2) + ac(\cos\beta)B(1,3) + bc(\cos\alpha)B(2,3)].$$

	x	*y*	*z*	B_{eq}
Zn(2)				
Zn	0	0.05447 (4)	¼	2.553 (7)
S	0.10484 (4)	0.13541 (7)	0.41786 (6)	3.40 (1)
N	0.0676 (1)	−0.1089 (2)	0.2090 (2)	2.47 (4)
C(1)	0.1765 (1)	0.0429 (3)	0.3575 (2)	3.41 (5)
C(2)	0.1467 (1)	−0.1063 (3)	0.3124 (2)	3.21 (5)
C(3)	0.0206 (1)	−0.2411 (3)	0.1985 (2)	2.51 (4)
C(4)	0.0677 (2)	−0.3769 (3)	0.2035 (3)	3.59 (6)
C(5)	0.0176 (2)	−0.5089 (3)	0.1955 (3)	4.72 (7)
C(6)	0.2562 (2)	0.0300 (4)	0.4671 (3)	5.08 (8)
C(7)	0.1870 (2)	0.1274 (4)	0.2453 (3)	5.00 (7)
Zn(3)				
Zn	0.95132 (8)	0.35116 (4)	0.95202 (6)	3.45 (1)
S(1)	1.1790 (2)	0.3745 (1)	0.9614 (2)	4.35 (4)
S(2)	0.8116 (2)	0.2693 (1)	1.0530 (2)	4.75 (4)
N(1)	0.9495 (5)	0.3605 (3)	0.7543 (4)	3.1 (1)
N(2)	0.7911 (5)	0.4344 (3)	0.9432 (4)	3.4 (1)
C(1)	1.1991 (7)	0.3361 (4)	0.8010 (6)	3.9 (2)
C(2)	1.0895 (7)	0.3734 (4)	0.7119 (6)	4.1 (2)
C(3)	0.8556 (8)	0.4258 (6)	0.7237 (6)	8.2 (2)
C(4)	0.8355 (7)	0.4426 (4)	0.5835 (6)	4.1 (2)
C(5)	0.7317 (9)	0.5045 (6)	0.5543 (7)	10.4 (3)
C(6)	0.644 (1)	0.5253 (6)	0.6352 (7)	12.5 (3)
C(7)	0.6643 (7)	0.5094 (4)	0.7746 (6)	4.7 (2)
C(8)	0.768 (1)	0.4482 (5)	0.8068 (6)	10.5 (2)
C(9)	0.6718 (7)	0.4039 (4)	1.0059 (8)	5.4 (2)
C(10)	0.7075 (7)	0.3480 (4)	1.1147 (6)	4.7 (2)
C(11)	1.3394 (7)	0.3619 (5)	0.7535 (8)	6.2 (2)
C(12)	1.1836 (8)	0.2487 (5)	0.8006 (8)	6.5 (2)
C(13)	0.783 (1)	0.3897 (5)	1.2213 (7)	8.7 (3)
C(14)	0.578 (1)	0.3135 (6)	1.164 (1)	12.1 (3)

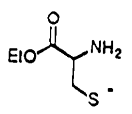
Zn(2) the molecules have point symmetry 2. The Zn atoms in each structure are ligated by two S and two N atoms from the tetradentate ligands to yield substantially distorted tetrahedral coordination geometries as evidenced by the angles with Zn as vertex which range from 85.6 (1) to 140.36 (3)° in Zn(2) and from 85.2 (1) to 134.35 (5)° in Zn(3). In Table 2 these coordination geometries are compared with those reported for Zn^II and Cu^II complexes of ligands (1*b*), (2) and (4)–(6), all of which contain MS$_2$(thiolate)$_2$N$_2$(amine)$_2$ chromophores. The M—S and M—N bond distances span narrow ranges and are relatively insensitive to the choice of metal or any additional constraints imposed by tetradentate *vs* bidentate ligation. The S—M—S′/N—M—N′ dihedral angles provide a measure of the deviation of the coordination geometries from tetrahedral (90°) or square planar (0°). The Zn complexes show deviations of approximately 10–30° from tetrahedral, with no obvious relationship of the deviation to the number of chelate rings. Apparently, the additional constraints imposed by the five-membered N,N chelate rings in Zn(2) and in Zn(3), which are reflected in the N—Zn—N′ angles, do not have a large effect on this measure of tetrahedrality. The Cu^II complexes Cu(1*b*) and Cu(2) show S—Cu—S′/N—Cu—N′ deviations of *ca* 20–30° from the square-planar value and much smaller S···S′ distances than in the Zn complexes. Indeed, in contrast to the Zn complexes, the S atoms in the Cu complexes are in close contact (the van der Waals diameter of S is 3.6 Å), which would hinder further movement of these atoms towards the electronically favored square-planar geometry.



(4)



(5)



(6)

The N,S chelate rings in Zn(2) and Zn(3) exhibit the envelope conformation with the tetrasubstituted C atoms [C(1), C(10)] comprising the flaps. In Zn(2), the N,N chelate ring adopts the *gauche* conformation. In contrast, the conformation of the corresponding N,N ring in Zn(3) is best described as an

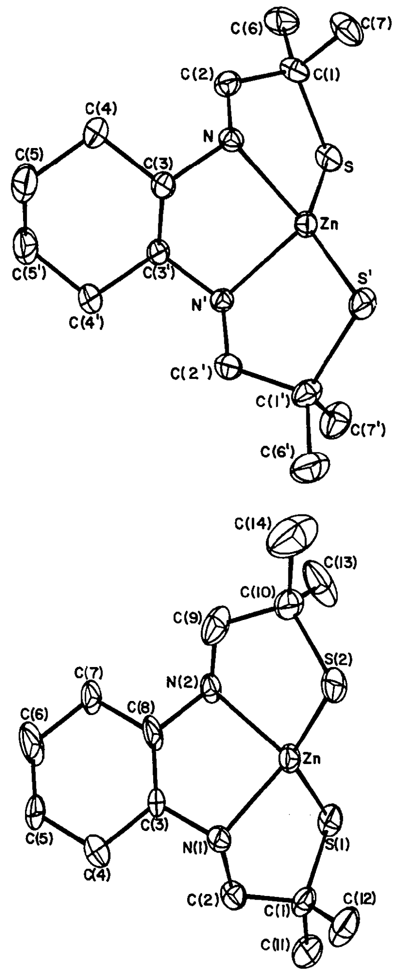


Fig. 1. Views of Zn(2) (top) and Zn(3) (bottom) showing the atom-numbering schemes. H atoms have been omitted for clarity.

Table 2. *Structural parameters of distorted tetrahedral* MS(*thiolate*)$_2$N(*amine*)$_2$ *chromophores* (M = Zn^{II}, Cu^{II})

	Zn(2)	Zn(3)	Cu(2)	Cu(1*b*)
M—S (Å)	2.2533 (6)	2.259 (1) 2.253 (1)	2.2317 (7) 2.2296 (6)	2.230 (5) 2.262 (4)
M—N (Å)	2.101 (2)	2.088 (4) 2.128 (4)	2.040 (2) 2.047 (2)	2.002 (11) 2.059 (13)
S—M—S′ (°)	140.36 (3)	134.35 (5)	106.64 (2)	98.6 (2)
N—M—N′ (°)	85.6 (1)	85.2 (1)	84.54 (7)	87.2 (5)
S—M—S′/N—M—N′ (°)*	70.99 (5)	63.4 (1)	32.77 (6)	21.0 (6)
S···S′ (Å)	4.240 (1)	4.159 (2)	3.5780 (9)	3.406 (6)
Ligand dentature	4, S–N–N–S	4, S–N–N–S	4, S–N–N–S	4, S–N–N–S
Chelate rings	5–5–5	5–5–5	5–5–5	5–5–5
Reference	This work	This work	(i)	(ii)

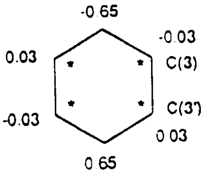
	Zn(4)$_2$	Na$_2$Zn(5)$_2$	Zn(6)$_2$
M—S (Å)	2.297 (4)	2.297 (1), 2.283 (1)	2.273 (1)
M—N (Å)	2.06 (1)	2.047 (3), 2.066 (3)	2.090 (1)
S—M—S′ (°)	137.1 (2)	133.4 (1), 132.0 (1)	124.6 (1)
N—M—N′ (°)	122.8 (6)	116.3 (2), 108.6 (2)	104.6 (1)
S—M—S′/N—M—N′ (°)	79.5 (3)	76.23 (8), 73.5 (1)	68.34 (3)
S···S′ (Å)	4.271 (6)	4.217 (2), 4.172 (2)	4.025 (2)
Ligand dentature	2, S–N	2, S–N	2, S–N
Chelate rings	5, 5	5, 5	5,5
Reference	(iii)	(iv)	(iv)

References: (i) Bharadwaj *et al.* (1992); (ii) Bharadwaj *et al.* (1986); (iii) Cohen, Mastropaolo, Potenza & Schugar (1978); (iv) Bell & Sheldrick (1984).

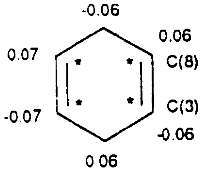
* Dihedral angle.

envelope that is nearly planar [with Zn, N(1) and N(2) defining the plane; C(8) and C(3) show deviations of 0.05 and −0.19 Å, respectively].

The cyclohexane ring in Zn(2) is typical in terms of bond distances [1.520 (3)–1.540 (4) Å], bond angles [110.5 (2)–112.2 (2)°] and conformation: the chair conformation is clearly indicated by deviations of atoms C(4) and C(4′) from the least-squares plane defined by the remaining cyclohexyl C atoms [see (7)].



(7)



(8)

In Zn(3), the six-membered ring is clearly a cyclohexa-1,4-diene with two C—C double bonds [1.298 (7), 1.278 (9) Å] and four C—C single bonds [1.499 (7)–1.512 (6) Å]. Interior angles with the vinyl C atoms as vertex [120.7 (5)–122.0 (5)°] are significantly larger than those with the methylene C atoms as vertex [114.0 (4), 115.2 (5)°], and both compare well with those reported for other substituted cyclohexa-1,4-dienes (Bennett & Purdham, 1978; Grossel, Cheetham, James & Newsam, 1980; Jandacek & Simonsen, 1969). In the solid state, cyclohexa-1,4-diene rings are found to be essentially planar (Gall, MacNicol, Mallinson & Welsh, 1985; Jandacek & Simonsen, 1969; Bennett & Purdham, 1978) or slightly puckered (Bennett & Purdham, 1978; Mez & Rihs, 1973). As indicated in (8), which shows deviations from the least-squares plane defined by the vinyl C atoms, the cyclohexadiene ring in Zn(3) is planar only to ±0.07 Å. Part of the deviation from planarity in this case may be an artifact arising from incorporation of a small amount of ligand (2) into the structure of Zn(3). The relatively large thermal parameters observed for the vinyl C atoms of the cyclohexadiene ring (Table 1) are consistent with this view.

The source of the purple color in Zn(3) is not known. If it were to arise from incorporation of Cu^{II}, based on the intensity of the color the level of doping must be small. Because the scattering factors of Cu and Zn are so similar, low-level substitution of Cu^{II} for Zn^{II} would not be crystallographically significant. Finally, the source of the cyclohexadiene-containing ligand (3) is puzzling. The presence of (3) was not apparent in the NMR spectra of solutions containing (2). Moreover, the isolation of neat Cu^{II}(2) (Bharadwaj *et al.*, 1992) did not reveal any oxidative dehydrogenation of (2).

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References

BELL, P. & SHELDRICK, W. S. (1984). *Z. Naturforsch. Teil B*, **39**, 1732–1737.

BENNETT, M. J. & PURDHAM, J. T. (1978). *Can J. Chem.* **56**, 1358–1363.

BHARADWAJ, P. K., FIKAR, R., POTENZA, M. N., ZHANG, X., POTENZA, J. A. & SCHUGAR, H. J. (1992). Manuscript in preparation.

BHARADWAJ, P. K., POTENZA, J. A. & SCHUGAR, H. J. (1986). *J. Am. Chem. Soc.* **108**, 1351–1352.

COHEN, B., MASTROPAOLO, D., POTENZA, J. A. & SCHUGAR, H. J. (1978). *Acta Cryst.* **B34**, 2859–2860.

Enraf–Nonius (1983). *Structure Determination Package*. Enraf–Nonius, Delft, The Netherlands.

GALL, J. H., MACNICOL, D. D., MALLINSON, P. R. & WELSH, P. A. (1985). *Tetrahedron Lett.* **26**, 4005–4008.

GROSSEL, M. C., CHEETHAM, A. K., JAMES, D. & NEWSAM, J. M. (1980). *J. Chem. Soc. Perkin Trans.* 2, pp. 471–475.

JANDACEK, J. & SIMONSEN, S. H. (1969). *J. Am. Chem. Soc.* **91**, 6663–6666.

KNAPP, S., KEENAN, T. P., ZHANG, X., FIKAR, R., POTENZA, J. A. & SCHUGAR, H. J. (1990). *J. Am. Chem. Soc.* **112**, 3452–3464.

MAIN, P., FISKE, S. J., HULL, S. E., LESSINGER, L., GERMAIN, G., DECLERCQ, J.-P. & WOOLFSON, M. M. (1982). *MULTAN82. A System of Computer Programs for the Automatic Solution of Crystal Structures from X-ray Diffraction Data.* Univs. of York, England, and Louvain, Belgium.

MARTIN, C. T., SCHOLES, C. P. & CHAN, S. I. (1988). *J. Biol. Chem.* **263**, 8420–8429.

MEZ, H.-C. & RIHS, G. (1973). *Helv. Chim. Acta*, **56**, 2766–2772.

SOLOMON, E. I., PENFIELD, K. W. & WILCOX, D. E. (1983). *Struct. Bonding (Berlin)*, **53**, 1–57.