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A second analysis of the crystal structure of copper(II) diethyldithiocarbamate.

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Vaciago and his co-workers, as part of their program of structural studies of the metal dithiocarbamates, have described an analysis and differential synthesis refinement of the crystal structure of copper(II) diethyldithiocarbamate (Bonamico, Dessy, Mugnoli, Vaciago & Zambonelli, 1965). While their work was in progress an independent study of the same structure was being pursued by the authors, the refinement being conducted by the block-diagonal least-squares method. Recently Vaciago and his colleagues have refined their published model by block-diagonal least-squares (Domenicano, Vaciago & Zambonelli, 1966; hereafter designated DVZ). As the least-squares refinements by DVZ (model A) and the authors (model B) are of similar precision, it is instructive to compare the models. It appears that where there are systematic errors in the intensity data the standard methods of estimating the accuracy of a structure analysis are of doubtful validity.

A large number of crystal samples were examined to select specimens for the model B analysis. All gave X-ray reflexions with shapes that were somewhat less than ideal. The best of those available were chosen for the collection of intensity data.

Eleven layers of [010]-axis data and four layers of [201]-axis data were collected by the multiple-film equi-inclination Weissenberg technique with Cu $K\alpha$ radiation. The reflexion intensities were estimated visually. The film factors were determined from the relative intensities of reflexions common to each pair of films. The data were corrected for absorption by the method of Busing & Levy (1957). A program written by Rae (1963) for the IBM 1620 computer was used to place the layers on a common scale. The final set of amplitudes comprised 3258 independent reflexions, of which 2368 were above film background.

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Table 1. *Atomic coordinates with e.s.d.'s* (× 10^4)

	x/a^A	x/a^B	y/b^A	y/b^B	z/c^A	z/c^B
Cu	1902 (1)	1902 (2)	318 (1)	318 (2)	644 (1)	643 (1)
S(1)	3349 (2)	3341 (4)	2115 (2)	2116 (2)	1107 (1)	1104 (2)
S(2)	2043 (2)	2039 (3)	618 (2)	620 (2)	2052 (1)	2053 (1)
S(3)	2462 (2)	2465 (4)	−332 (2)	−333 (2)	−507 (1)	−509 (2)
S(4)	768 (2)	769 (3)	−1647 (2)	−1652 (2)	280 (1)	279 (1)
N(1)	3739 (6)	3741 (10)	2640 (6)	2631 (8)	2769 (3)	2771 (5)
N(2)	1366 (5)	1371 (8)	−2654 (5)	−2636 (7)	−1032 (3)	−1027 (5)
C(1)	3108 (6)	3131 (10)	1887 (7)	1884 (8)	2067 (4)	2075 (6)
C(2)	4602 (8)	4644 (12)	3730 (9)	3741 (11)	2747 (5)	2761 (8)
C(3)	3551 (8)	3534 (13)	2420 (8)	2412 (11)	3588 (4)	3596 (6)
C(4)	3620 (10)	3681 (16)	4875 (10)	4875 (11)	2403 (6)	2418 (8)
C(5)	4811 (11)	4759 (15)	1654 (11)	1637 (14)	4239 (6)	4239 (9)
C(6)	1519 (7)	1502 (10)	−1679 (6)	−1684 (8)	−504 (4)	−499 (6)
C(7)	2093 (8)	2117 (12)	−2672 (8)	−2672 (10)	−1646 (4)	−1643 (7)
C(8)	475 (8)	467 (12)	−3754 (8)	−3752 (10)	−1040 (5)	−1039 (7)
C(9)	1057 (10)	1026 (17)	−2302 (10)	−2296 (13)	−2565 (5)	−2580 (8)
C(10)	1370 (11)	1382 (16)	−4817 (9)	−4815 (10)	−498 (7)	−495 (10)

Table 2. *Anisotropic temperature coefficients with e.s.d.'s* (× 10^4)*

	b_{11}^A	b_{11}^B	b_{22}^A	b_{22}^B	b_{33}^A	b_{33}^B	b_{12}^A	b_{12}^B	b_{13}^A	b_{13}^B	b_{23}^A	b_{23}^B
Cu	131 (1)	173 (2)	76 (1)	74 (1)	29 (–)	40 (1)	−25 (2)	−28 (2)	61 (1)	81 (2)	−14 (1)	−15 (1)
S(1)	137 (2)	171 (4)	96 (2)	91 (2)	37 (1)	46 (1)	−51 (3)	−48 (5)	69 (1)	87 (3)	−10 (2)	−10 (3)
S(2)	124 (2)	162 (3)	77 (1)	66 (2)	31 (1)	40 (1)	−29 (3)	−27 (4)	54 (1)	69 (3)	−11 (1)	−9 (2)
S(3)	213 (2)	249 (5)	83 (2)	71 (2)	53 (1)	57 (1)	−82 (3)	−86 (5)	153 (1)	155 (4)	−32 (2)	−31 (3)
S(4)	125 (1)	162 (3)	78 (1)	75 (2)	28 (1)	36 (1)	−13 (3)	−10 (4)	62 (1)	82 (3)	−3 (1)	−2 (2)
N(1)	106 (5)	161 (12)	86 (5)	81 (8)	35 (2)	44 (4)	−20 (10)	−69 (16)	39 (5)	51 (11)	−33 (5)	−28 (9)
N(2)	106 (5)	144 (11)	70 (5)	65 (7)	34 (2)	42 (3)	−9 (9)	−44 (14)	56 (4)	67 (10)	−19 (5)	−6 (8)
C(1)	86 (5)	119 (11)	86 (6)	61 (7)	33 (2)	40 (4)	6 (11)	14 (14)	38 (5)	39 (10)	−8 (6)	6 (8)
C(2)	129 (7)	179 (16)	123 (8)	102 (11)	46 (3)	57 (6)	−95 (14)	−122 (22)	47 (7)	93 (16)	−41 (8)	−31 (13)
C(3)	152 (7)	192 (17)	111 (7)	112 (12)	36 (2)	38 (4)	−17 (14)	14 (23)	68 (6)	72 (14)	−29 (7)	−21 (11)
C(4)	181 (9)	249 (23)	101 (7)	88 (10)	72 (4)	65 (5)	−106 (15)	−80 (25)	117 (8)	113 (20)	−32 (9)	−27 (13)
C(5)	199 (12)	200 (21)	168 (11)	178 (17)	42 (3)	61 (6)	−19 (22)	28 (30)	46 (10)	68 (19)	−9 (10)	9 (17)
C(6)	111 (6)	144 (13)	68 (5)	49 (7)	28 (2)	38 (4)	1 (11)	9 (15)	44 (5)	54 (11)	1 (5)	7 (8)
C(7)	152 (7)	181 (16)	110 (7)	90 (11)	37 (2)	56 (5)	17 (13)	−15 (22)	86 (5)	113 (16)	−27 (6)	−21 (12)
C(8)	131 (7)	181 (16)	99 (7)	70 (9)	41 (2)	52 (5)	−13 (14)	−58 (20)	52 (6)	72 (14)	−22 (7)	−22 (11)
C(9)	225 (11)	306 (26)	157 (10)	146 (15)	38 (2)	44 (5)	−51 (19)	−99 (32)	96 (7)	151 (20)	−21 (9)	−27 (14)
C(10)	210 (10)	245 (24)	88 (7)	75 (10)	81 (4)	82 (8)	−6 (17)	11 (25)	137 (9)	130 (24)	10 (10)	14 (15)

* Coefficients defined such that the atomic temperature factor is in the form
$\exp\{-10^4(b_{11}h^2+b_{22}k^2+b_{33}l^2+b_{12}hk+b_{13}hl+b_{23}kl)\}$.

The structure was solved by three-dimensional Patterson and electron density syntheses. The non-hydrogen atomic parameters, three positional and six thermal per atom, and the scale factor were refined by the block-diagonal least-squares method. The quantity $\Sigma\, w(|F_o|-|F_c|)^2$ was minimized during the refinement. The weighting factor w was expressed as

$$w=1/[1+(|F_o|-b)^2/a^2]\,,$$

the constants a and b being derived from a plot of $\{(F_o-F_c)^2-1\}^{\frac{1}{2}}$ *versus* $|F_o|$. The scattering factors used were those listed in *International Tables for X-ray Crystallography* (1962), modified to take into account the reasonance structure of the molecule. Accordingly the functions for $S^{0{\cdot}7+}$ and $N^{0{\cdot}4-}$ were prepared by linear interpolation between the appropriate neutral and ionic values. Corrections for the real components of the anomalous dispersion contributions (Dauben & Templeton, 1955) were applied to the copper and sulphur scattering factors. At the completion of the refinement the R index, defined as $\Sigma\,||F_o|-|F_c||/\Sigma\,|F_o|$ for all reflexions except those unobserved with F_c less than the limit of observation, was 0·110. A list of the observed and calculated structure factors has been deposited in the library at the University of Western Australia. Copies are available on request.

Crystal data

$Cu[(C_2H_5)_2NCS_2]_2$
F.W. 360·08
Space group, $P2_1/c$ (monoclinic)
$Z=4$

Cell dimensions:*

$a=10{\cdot}4$, $b=10{\cdot}7$, $c=16{\cdot}8$ Å
$\beta=113°$

$D_m=1{\cdot}48$ g.cm^{-3}, by flotation
$D_x=1{\cdot}498$.

The final positional and thermal parameters are listed in Tables 1 and 2 respectively, together with the values given by DVZ. The parameter standard deviations are those estimated by inverting the normal equations matrix for each model. The superscripts in Tables 1 and 2 denote the model to which the particular parameter is related. The bond distances and corresponding standard deviations are given in Table 3.

Table 3. *Bond lengths with e.s.d's*

	Model A	Model B
Cu–S(1)	2·324 (2) Å	2·321 (3)
Cu–S(2)	2·305 (2)	2·310 (3)
Cu–S(3)	2·300 (2)	2·305 (4)
Cu–S(4)	2·332 (2)	2·336 (3)
S(1)–C(1)	1·721 (8)	1·724 (12)
S(2)–C(1)	1·706 (7)	1·716 (10)
S(3)–C(6)	1·710 (7)	1·728 (10)
S(4)–C(6)	1·741 (8)	1·718 (12)
C(1)–N(1)	1·341 (8)	1·328 (12)
C(6)–N(2)	1·325 (8)	1·310 (12)
N(1)–C(2)	1·449 (11)	1·485 (15)
N(1)–C(3)	1·463 (10)	1·482 (15)
N(2)–C(7)	1·466 (10)	1·484 (17)
N(2)–C(8)	1·462 (10)	1·481 (14)
C(2)–C(4)	1·518 (13)	1·499 (17)
C(3)–C(5)	1·515 (12)	1·497 (16)
C(7)–C(9)	1·505 (9)	1·544 (15)
C(8)–C(10)	1·492 (12)	1·499 (15)

The results of the authors' analysis in general confirm those of DVZ but there are differences in detail. The mean deviation in a non-hydrogen atomic position is 0·020 Å, and the largest discrepancy is 0·055 Å for atom C(4). For the bond distances there is a mean deviation of 0·015 Å and the largest difference is 0·039 Å for C(7)–C(9).

In order to compare the agreement between models A and B on a statistical basis we consider the Δ/σ ratios for the parameter differences, where Δ/σ for some structural parameter u_i is given by

$$\frac{u_i\,(\text{model A})-u_i\,(\text{model B})}{\{\sigma^2[u_i\,(\text{model A})]+\sigma^2[u_i\,(\text{model B})]\}^{\frac{1}{2}}}\,.$$

It follows that for a set of n independent discrete variables the quantity

$$T^2=\sum_{i=1}^{n}\,(\Delta/\sigma)_i^2$$

is distributed as χ^2 with n degrees of freedom.

The Δ/σ values for the positional and thermal parameters are listed in Tables 4 and 5 respectively. On the sound assumption that the covariance terms involving the atomic coordinates are negligible, T^2 is 74·32 for the fifty-one atomic coordinates. The corresponding probability that the two sets of positions are random normal variations from the parent distribution is 0·023, *i.e.* the coordinates are in agreement at the significance level of 2·3 %. This casts some doubt on the estimates of accuracy for the analyses. However, it should be noted that the coordinate standard deviation need only have been slightly underestimated. If the coordinate standard deviation estimates are too small by a factor of 1·10, for example, the corresponding agreement level rises to 50·0 %.

Table 4. *Δ/σ values for the atomic coordinates*

	$\Delta/\sigma\ (x/a)$	$\Delta/\sigma\ (y/b)$	$\Delta/\sigma\ (z/c)$
Cu	0·00	0·00	0·71
S(1)	1·79	−0·35	1·34
S(2)	1·11	−0·71	−0·71
S(3)	−0·67	0·35	0·89
S(4)	−0·28	1·77	0·71
N(1)	−1·71	0·90	−0·34
N(2)	−0·53	−2·09	−0·86
C(1)	−1·97	0·28	−1·11
C(2)	−2·91	−0·77	−1·48
C(3)	1·11	0·59	−1·11
C(4)	−3·23	0·00	−1·50
C(5)	2·79	0·96	0·00
C(6)	1·39	0·50	−0·69
C(7)	−1·66	0·00	−0·37
C(8)	0·55	−0·16	−0·12
C(9)	1·57	−0·37	1·59
C(10)	−0·62	−0·15	−0·25

There are large systematic differences between the b_{ij} sets which could be partly accounted for in terms of differing degrees of disorder in the crystals used for the two analyses since the Δb_{ij}'s are almost all pcsitive for b_{22} and negative for b_{11} and b_{33}. Also there are generally smaller vibration parameters for model A which is consistent with there being no absorption corrections applied to the data of DVZ.

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* The cell dimensions given by Bonamico *et al.* are more accurate than those determined by the authors. Consequently the more precise values have been used in calculating molecular dimensions for this communication.

Table 5. *Δ/σ values for the temperature coefficients*

	$\Delta/\sigma\ (b_{11})$	$\Delta/\sigma\ (b_{22})$	$\Delta/\sigma\ (b_{33})$	$\Delta/\sigma\ (b_{12})$	$\Delta/\sigma\ (b_{13})$	$\Delta/\sigma\ (b_{23})$
Cu	−18·75	1·42	−11·00	1·06	−8·94	0·71
S(1)	−7·61	1·77	−6·38	−0·51	−5·70	0·00
S(2)	−10·53	4·91	−6·38	−0·40	−4·75	−0·89
S(3)	−6·68	4·24	−2·84	0·69	−0·49	−0·28
S(4)	−11·71	1·34	−5·68	−0·60	−6·33	−0·45
N(1)	−4·23	0·53	−2·01	2·60	−0·99	−0·49
N(2)	−3·14	0·58	−2·22	2·10	−1·02	−1·38
C(1)	−2·73	2·71	−1·57	−0·45	−0·09	−1·40
C(2)	−2·86	1·54	−1·64	1·04	−2·63	−0·66
C(3)	−2·18	−0·07	−0·45	−1·15	−0·26	−0·61
C(4)	−2·75	1·06	1·09	−0·89	0·19	−0·32
C(5)	−0·04	−0·49	−2·83	−1·26	−1·02	−0·91
C(6)	−2·30	2·21	−2·24	−0·43	−0·83	−0·64
C(7)	−1·66	1·53	−3·53	1·25	−1·61	−0·45
C(8)	−2·86	2·54	−2·04	1·84	−1·31	0·00
C(9)	−2·87	0·61	−1·11	1·29	−2·60	0·36
C(10)	−1·35	1·06	−0·11	−0·56	0·27	−0·22

The case is similar to others discussed recently by O'Connell (1965) who has shown that systematic errors in the intensity data or a poor choice of weighting function in the refinement may give rise to apparently significant differences from the correct structure. This results from the lack of validity of the assumption, made in assessing the standard deviations from the least-squares matrix, that the errors are predominantly random in character. O'Connell has shown that systematic data errors can arise from a tendency to overestimate the strengths of the weaker spots in photographic data. Although the errors in the individual measurements are small they result in film-factor errors which are cumulative, giving rise to large inaccuracies in the stronger intensities.

A comparison of the intra-pack film factor calculations for the model B data with more recent measurements by a photometric technique suggests that the film factors were slightly underestimated, but it is impossible to verify this by remeasurement of the original films because of the irregular spot shape. Moreover this type of error cannot account for all the discrepancies in the b_{ij}'s, since the Δb_{22}'s are in the opposite direction to that required. It may well be that the difference in the b_{ij}'s and the errors in the parameter standard deviations result from a combination of differing crystal disorder, absorption effects and film factor and spot shape errors. It is clear, however, that little attention can be paid to the absolute magnitude of the b_{ij}'s, and that the standard deviations in the positional parameters must be regarded as an under-estimate. It seems probable, moreover, that errors of the type discussed above are by no means uncommon in structure analysis.

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X-ray powder data of *T* phases composed of aluminum and magnesium with silver copper or zinc.

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Ternary compounds designated *T* phases are found in age hardening alloys of aluminum and magnesium with silver, copper or zinc. These phases have a body-centered cubic lattice with a parameter of about 14 Å. The structure of the *T* phase in the Al–Mg–Zn system has been determined by Bergman, Waugh & Pauling (1957) who showed it to contain 162 atoms per unit cell corresponding to the formula $Mg_{32}(Al,Zn)_{49}$. The corresponding phase containing copper has been given the formulae Mg_4CuAl_6 (Laves, Löhberg & Witte, 1935) and Mg_4CuAl_5 (Nishimura, 1937) based on approximations to composition. In investigations of the effect of silver additions to aluminum–magnesium alloys, a *T* phase has also been found in this system by Wheeler, Blankenburgs & Staddon (1965) and independently by ourselves; in each case compositions made to the formula Mg_4AgAl_6 were not entirely single-phase.

As powder data were required by us for investigations on age hardening, compounds of each of the *T* phases