Ir. In Table III a (rather rough) separation is made between high and low frequencies, the corresponding ligands being classified as hard and soft, respectively. A further study of these infrared correlations may need a more subtle nomenclature. The oxidation number and the corresponding coordination symmetry of the gold seem to have (only) little influence on the gold–halogen stretching frequencies.

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# Structure and Properties of Dibromo-N,N-di-*n*-butyldithiocarbamato Complexes of Copper(III) and Gold(III)

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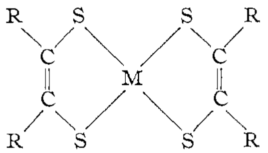
Preparation, crystal structure, and some magnetic and spectral properties of dibromo-N,N-di-*n*-butyldithiocarbamatocopper(III) and -gold(III), $CuBr_2S_2CN(n\text{-}C_4H_9)_2$ and $AuBr_2S_2CN(n\text{-}C_4H_9)_2$, are reported. These compounds form isomorphous crystals in the monoclinic space group C2/c. The cell dimensions measured from photographs are: $a = 13.85 \pm 0.03$, $b = 14.94 \pm 0.03$, $c = 7.28 \pm 0.02$ Å, $\beta = 98.8 \pm 0.3°$ for the copper compound and $a = 13.85 \pm 0.03$, $b = 14.94 \pm 0.03$, $c = 7.41 \pm 0.02$ Å, $\beta = 98.8 \pm 0.3°$ for the gold compound, with four molecules per unit cell. The crystal structure of the copper compound has been determined by a three-dimensional X-ray analysis. About 780 intensities were measured photometrically from equiinclination Weissenberg photographs. The structural parameters were refined by least-squares methods to a conventional $R$ factor of 0.10. The ismorphous gold compound was refined in projection with 94 $hk0$ intensities until the $R$ factor was 0.09. The compounds have Cu(III) and Au(III) in a planar fourfold coordination with two Br and two S. The Cu–S and the Cu–Br distances of 2.193 ± 0.006 and 2.311 ± 0.004 Å, respectively, are significantly smaller than those in Cu(II) compounds. This suggests an appreciable ionic contribution in the copper–ligand bonding. The diamagnetic behavior of these compounds is in accord with a low-spin $d^8$ configuration.

## Introduction

During our work on the redox properties of dithiocarbamato complexes of transition metals we succeeded in synthesizing $CuBr_2(dtc)$ (dtc = N,N-di-*n*-butyldithiocarbamate = $S_2CN(C_4H_9)_2$) by a reaction analogous[1,2] to the preparation of $AuBr_2(dtc)$: $Cu(dtc) + Br_2 \rightarrow CuBr_2(dtc)$. This $CuBr_2(dtc)$ belongs to the very small group of Cu(III) compounds. Only potassium hexafluorocuprate(III), the alkaline earth and alkali cuprates(III), some periodato and tellurato complexes,[3] and the recently reported bisbiuretato complex[4] have been identified as Cu(III) compounds. In the series of planar complexes of the type



the significance of the oxidation number of the metal has been subject to discussion because the highest filled orbitals in these complexes have appreciable ligand character. We think the formal concept of oxidation number is however still appropriate for nomenclature purposes and for an easy counting of electrons. In this formal sense it can be said that Cu(III) complexes are known with bis(trifluoromethyl)-1,2-dithieten,[5] benzene-1,2-dithiolate,[6] and maleonitriledithiolate.[7] The compound $CuBr_2(dtc)$ having a lower coordination symmetry than the former compounds seems to be an interesting new member of the Cu(III) family. We report the crystal structure and some magnetic and spectral properties of it as well as of the isomorphous $AuBr_2(dtc)$.

Converting Cu(dtc) with 0.5 mol of $Br_2$ a compound of stoichiometric composition CuBr(dtc) is formed. On account of its paramagnetic character it seems to be a Cu(II) compound which is in contrast with the gold compound of similar composition, reported[8] to be $Au(dtc)_2{}^+AuBr_2{}^-$ with Au(III) and Au(I), respectively. Structural studies of this CuBr(dtc) are in progress.

## Experimental Section[9]

**Preparation of the Complexes.**—Cu(dtc) was prepared from copper powder (Merck, electrolytically prepared) and tetra-*n*-butylthiuram disulfide (Fluka Praktikum) according to Åkerström.[10]

**$CuBr_2(dtc)$** was prepared from a solution of Cu(dtc) in carbon disulfide (25 mg/ml) which was converted at room temperature

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(1) H. J. A. Blaauw, R. J. F. Nivard, and G. J. M. van der Kerk, *J. Organometal. Chem.* (Amsterdam), **2**, 236 (1964).

(2) Cu(dtc) and Au(dtc) are polymeric in solution (see ref 3). Monomeric formulas are used for the sake of simplicity.

(3) "Gmelin's Handbuch der Anorganische Chemie, Kupfer, Teil B," 3rd ed, Verlag Chemie G.m.b.H., Weinheim, Germany, 1965, pp 1407, 1451.

(4) J. J. Bour and J. J. Steggerda, *Chem. Commun.*, 85 (1967).

(5) A. Davison, D. V. Howe, and E. T. Shawl, *Inorg. Chem.*, **6**, 458 (1967).

(6) M. J. Baker-Hawkes, E. Billig, and H. B. Gray, *J. Am. Chem. Soc.*, **88**, 4870 (1966).

(7) J. D. Forrester, A. Zalkin, and D. H. Templeton, *Inorg. Chem.*, **3**, 1507 (1964).

(8) P. T. Beurskens, H. J. A. Blaauw, J. A. Cras, and J. J. Steggerda, *Inorg. Chem.*, **7**, 805 (1968).

(9) We gratefully acknowledge the assistance of Mr. G. M. G. M. van Lieshout in the preparative work and of Mr. W. P. J. H. Bosman in the X-ray crystallographic analysis.

(10) S. Åkerström, *Arkiv Kemi*, **14**, 395 (1966).

TABLE I

ATOMIC PARAMETERS FOR $CuBr_2$(dtc) WITH STANDARD DEVIATIONS[a]

| | x | y | z | $\beta_{11}$ | $\beta_{22}$ | $\beta_{33}$ | $\beta_{12}$ | $\beta_{13}$ | $\beta_{23}$ |
|---|---|---|---|---|---|---|---|---|---|
| Cu | .0000 | -.0607( 2) | -.2500 | .0063( 3) | .0029( 2) | .0031(22) | .0000 | .0025( 3) | .0000 |
| Br | .1263( 2) | -.1568( 1) | -.1388( 3) | .0069( 1) | .0035( 1) | .0068(21) | .0009( 1) | .0027( 2) | .0006( 2) |
| S | .0902( 3) | .0550( 3) | -.1491( 6) | .0046( 3) | .0027( 2) | .0060(23) | .0001( 2) | .0023( 4) | -.0001( 3) |
| N | .0000 | .2114(13) | -.2500 | .0029(11) | .0029( 9) | .0059(47) | .0000 | .0014(17) | .0000 |
| C(1) | .0000 | .1234(18) | -.2500 | .0044(16) | .0037(13) | .0195(74) | .0000 | .0032(30) | .0000 |
| C(2) | .0870(15) | .2601(15) | -.1590(32) | .0030(10) | .0049(11) | .0237(55) | -.0011( 9) | -.0011(19) | -.0062(20) |
| C(3) | .0642(14) | .3292(11) | -.0211(25) | .0043(10) | .0026( 8) | .0085(37) | -.0007( 7) | .0017(15) | -.0009(12) |
| C(4) | .1599(16) | .3703(13) | .0811(27) | .0056(13) | .0031( 9) | .0120(43) | -.0007( 8) | .0001(19) | .0015(15) |
| C(5) | .1458(22) | .4451(18) | .2195(32) | .0098(21) | .0065(15) | .0116(50) | .0011(14) | .0029(25) | -.0041(20) |

[a] The key to atomic numbering is given in Figure 2. The estimated standard deviations given in parentheses are the result of the least-squares refinement. The expression used for the temperature factors is: $\exp[-(\beta_{11}h^2 + \beta_{22}k^2 + \beta_{33}l^2 + 2\beta_{12}hk + 2\beta_{13}hl + 2\beta_{23}kl)$, the components of the mean-square displacements of the atoms being $9.49\beta_{11}$, $11.31\beta_{22}$, and $2.622\beta_{33}$ Å$^2$.

with an equimolar amount of $Br_2$ (as a 100-mg/ml solution in carbon disulfide). After adding an equal volume of diethyl ether and cooling at 0° for 10 hr, a precipitate was formed. This was filtered and purified by dissolving in chloroform or methylene chloride and reprecipitating with an equal volume of diethyl ether. An 80% yield was obtained as dark violet, needle-shaped crystals; mp 98.5–100° (uncor). *Anal.* Calcd for $CuBr_2S_2CN(C_4H_9)_2$: Cu, 14.9; Br, 37.4; C, 25.3; H, 4.24. Found: Cu, 15.1; Br, 37.1; C, 25.1; H, 4.15. $CuBr_2$(dtc) is soluble in chloroform, methylene dichloride, and benzene, slightly soluble in carbon disulfide, and insoluble in diethyl ether. The solid substance is stable in air at room temperature. Solutions in chloroform and methylene chloride however change from pink to brown in a few days. Solutions in acetonitrile and acetone are very unstable: a turbidity appears after some minutes, especially when some water is added.

$AuBr_2$(dtc) was prepared from Au(dtc) and $Br_2$ according to Blaauw.[1]

**Spectroscopy.**—Ultraviolet spectra were measured in methylene chloride solutions using a Cary 14 instrument. Infrared spectra of $CuBr_2$(dtc) and Cu(dtc) in the region 5000–650 cm$^{-1}$ were measured with a Beckman IR4 double-beam instrument; all specimens were examined in KBr pellets.

**Magnetic Susceptibility.**—This was measured at room temperature with a standard Gouy-type balance.

**Three-Dimensional X-Ray Crystal Structure Analysis of $CuBr_2$(dtc).**—The compound $CuBr_2$(dtc) crystallizes in the monoclinic system as prismatic needles along the *c* axis. A crystal of 0.1 × 0.1 × 1.0 mm$^3$ was used for oscillation (around the *c* axis), equiinclination Weissenberg (*hk*0 through *hk*6), and precession (*h*0*l* through *h*2*l*) photographs with nickel-filtered Cu K$\alpha$ radition (1.5418 Å). For measurement of the cell parameters oscillation and Weissenberg diagrams were superimposed by copper diffraction lines for calibration. The cell dimensions at 20° and their root-mean-square errors (calculated from the experimental errors) are: $a = 13.85 \pm 0.03$, $b = 14.94 \pm 0.03$, $c = 7.28 \pm 0.02$ Å, $\beta = 98.8 \pm 0.3°$, $V = 1488 \pm 7$ Å$^3$, $Z = 4$. The systematic extinctions are: for *hkl*, $h + k = 2n + 1$; for *h*0*l*, $l = 2n + 1$ ($h = 2n + 1$), which are compatible only with the space groups Cc and C2/c. Successful determination of the structure was possible assuming the crystal to be centrosymmetric, space group C2/c. Three-dimensional intensity data were collected from seven layers of vertically integrated Weissenberg photographs, using the multiple-film technique. Of the 1150 attainable symmetry-independent reflections, 780 reflections were measured with an optical densitometer and another 200 reflections were estimated visually (slightly above film background). The intensities were corrected for Lorentz, polarization, and Philips factors. No absorption correction was applied ($\mu R = 0.7$; maximum effect on the intensities, 20%). The seven layers were scaled by Wilson's statistical method.

The structure was solved by Patterson and Fourier[11] methods. The molecule is situated on a twofold axis. All atoms except hydrogen atoms could be located and the structure was refined by full-matrix least-squares methods.[12] The function that was minimized is: $\Sigma w(|F_o| - |F_c|)^2$. The weight $w$ for each reflection was calculated as $w = n/(20 + |F_o| + 0.04|F_o|^2)$ with $n = 1$ for the 780 measured reflections, $n = 0.25$ for the 200 visually estimated reflections, and $n = 0$ for the zero-observed reflections and for some unreliable or extinction reflections. The atomic scattering factors were those of the neutral atoms, corrected for anomalous scattering ($\Delta f'$), using data from the "International Tables for X-Ray Crystallography." The conventional $R$ factor is defined as $R = \Sigma(|F_o| - |F_c|)/\Sigma|F_o|$ for the 780 measured reflections; values given in parentheses include the 200 visually estimated reflections. After refinement of the seven scale factors and the positional and individual isotropic temperature factor parameters of all atoms, the $R$ factor was 0.13 (0.15). Further refinement with anisotropic temperature parameters for all atoms and with fixed scale factors gave $R = 0.10$ (0.13). Finally the scale factors were included again with fixed temperature factors for the nitrogen and carbon atoms, and for the copper, bromine, and sulfur atoms in alternating cycles, causing only negligible changes in the $R$ factor and in the positional and vibrational parameters, except for an over-all decrease of the vibrational amplitudes along the *c* axis. The vibrational parameters along *c* ($\beta_{33}$) will have no physical significance because of the high correlation coefficients (up to 0.98) between these parameters and the scale factors. The physical significance of the remaining anisotropic temperature factor parameters is reduced by the lack of an absorption correction. The final difference Fourier synthesis showed eight maxima of 0.4–0.7 electron/Å$^3$, four of which correspond to calculated positions of hydrogen atoms. The remaining five hydrogens could not be located on this map and therefore no hydrogen atoms were included in the calculations.

**Two-Dimensional X-Ray Analysis of $AuBr_2$(dtc).**—Freshly crystallized $AuBr_2$(dtc) is isomorphous with the copper compound, space group C2/c. Cell dimensions and two-dimensional intensity data were obtained as described for the copper com-

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(11) A Fourier program and some data-handling programs for the IBM 360/40 computer were specially written for this research.

(12) The program ORFLS by Busing, Martin, and Levy (1962) was used on an IBM 360/40 computer.

Table II

Observed and Calculated Structure Factors for $CuBr_2$(dtc)[a]

| | | |
|---|---|---|
| H, | K=0 | L=0 |
| 2 | 175 | 216 |
| 4 | 240 | -216 |
| 6 | 34 | 25 |
| 8 | 190 | 159 |
| 10 | 78 | 61 |
| 12 | 9* | 18 |
| 14 | 34 | 31 |
| 16 | 22 | 15 |
| H, | K=1 | L=0 |
| 1 | 144R | 255 |
| 3 | 67 | 45 |
| 5 | 69 | -53 |
| 7 | 82 | 69 |
| 9 | 133 | 112 |
| 11 | 47 | 37 |
| 13 | 7* | 8 |
| 15 | 20 | 13 |
| H, | K=2 | L=0 |
| 2 | 43 | 46 |
| 4 | 84 | 78 |
| 6 | 25 | 22 |
| 8 | 14 | -9 |
| 10 | 42 | 33 |
| 12 | 55 | 42 |
| 16 | 24 | -14 |
| H, | K=3 | L=0 |
| 1 | 59 | -60 |
| 3 | 145 | 157 |
| 5 | 92 | 82 |
| 7 | 130 | -125 |
| 9 | 76 | -65 |
| 11 | 87 | 72 |
| 13 | 51 | 42 |
| 15 | 26 | -23 |
| 17 | 5* | -13 |
| H, | K=4 | L=0 |
| 0 | 141 | -150 |
| 2 | 35 | 27 |
| 4 | 116 | 116 |
| 6 | 53 | -48 |
| 8 | 79 | -72 |
| 10 | 33 | 30 |
| 12 | 48 | 43 |
| 14 | 20 | -19 |
| H, | K=5 | L=0 |
| 1 | 23 | -13 |
| 3 | 67 | -65 |
| 5 | 20 | -19 |
| 7 | 40 | 29 |
| 11 | 22 | -19 |
| 13 | 15* | -14 |
| H, | K=6 | L=0 |
| 0 | 79 | 79 |
| 2 | 61 | -61 |
| 4 | 147 | -154 |
| 6 | 4* | -5 |
| 8 | 63 | 55 |
| 10 | 45 | -45 |
| 12 | 80 | -71 |
| 16 | 19 | 25 |
| H, | K=7 | L=0 |
| 1 | 20 | -18 |
| 3 | 142 | -148 |
| 5 | 90 | -93 |
| 7 | 54 | 47 |
| 11 | 86 | -78 |
| 13 | 41 | -37 |
| 15 | 7* | 15 |
| H, | K=8 | L=0 |
| 0 | 113 | -117 |
| 2 | 86 | -91 |
| 4 | 23 | -19 |
| 6 | 31 | 13 |
| 8 | 31 | -27 |
| 10 | 52 | -47 |
| 12 | 27 | -23 |
| H, | K=9 | L=0 |
| 1 | 144 | -160 |
| 3 | 48 | 47 |
| 5 | 78 | 77 |
| 7 | 50 | -51 |
| 9 | 79 | -75 |
| 11 | 17 | -16 |
| H, | K=10 | L=0 |
| 0 | 174 | -220 |
| 2 | 51 | -50 |
| 4 | 97 | 109 |
| 6 | 4* | 8 |
| 8 | 72 | -70 |
| 10 | 27 | -24 |
| 12 | 6* | 1 |
| H, | K=11 | L=0 |
| 1 | 62 | -63 |
| 3 | 17 | -23 |
| 7 | 7* | -5 |
| 9 | 20 | -23 |
| 11 | 12* | -14 |
| 13 | 9* | -12 |
| H, | K=12 | L=0 |
| 0 | 28 | 35 |
| 2 | 7* | -9 |
| 4 | 57 | -58 |
| 6 | 14* | -17 |
| 8 | 19 | 27 |
| 10 | 6* | -10 |
| 12 | 31 | -36 |
| H, | K=13 | L=0 |
| 1 | 42 | 51 |
| 3 | 45 | -55 |
| 5 | 23 | -28 |
| 7 | 45 | 56 |
| 9 | 22 | 25 |
| 11 | 28 | -28 |
| H, | K=14 | L=0 |
| 0 | 31 | 44 |
| 2 | 7* | 11 |
| 4 | 5* | -4 |
| 6 | 29 | 30 |
| 8 | 27 | 30 |
| H, | K=15 | L=0 |
| 1 | 10* | 14 |
| 3 | 43 | 53 |
| 5 | 25 | 26 |
| 7 | 12* | -16 |
| H, | K=16 | L=0 |
| 2 | 25 | 26 |
| 4 | 38 | 46 |
| 8 | 16 | -20 |
| H, | K=17 | L=0 |
| 1 | 5* | 10 |
| 3 | 28 | 31 |
| 5 | 5* | 9 |
| 7 | 4* | -12 |
| H, | K=18 | L=0 |
| 0 | 48 | 54 |
| 2 | 27 | 27 |
| 4 | 5* | -14 |
| H, | K=19 | L=0 |
| 1 | 30 | 48 |
| H, | K=1 | L=1 |
| -17 | 22 | -19 |
| -13 | 53 | 50 |
| -11 | 19 | 13 |
| -9 | 107 | -96 |
| -7 | 64 | -57 |
| -5 | 134 | 122 |
| -3 | 131 | 112 |
| -1 | 89 | -102 |
| 1 | 53 | -33 |
| 3 | 125 | 128 |
| 5 | 66 | -50 |
| 7 | 139 | -140 |
| 9 | 25 | 23 |
| 11 | 89 | 84 |
| H, | K=2 | L=1 |
| -16 | 32 | -27 |
| -14 | 11* | 20 |
| -12 | 72 | 67 |
| -10 | 57 | -47 |
| -8 | 93R | -143 |
| -6 | 34 | 33 |
| -4 | 96 | 82 |
| -2 | 186 | -191 |
| 0 | 106 | -119 |
| 2 | 116 | 126 |
| 4 | 38 | 29 |
| 6 | 122 | -118 |
| 8 | 76 | -61 |
| 10 | 50 | 42 |
| 12 | 26 | 23 |
| 14 | 35 | -32 |
| H, | K=3 | L=1 |
| -17 | 19 | -17 |
| -15 | 7* | -14 |
| -9 | 63 | -52 |
| -7 | 118 | -109 |
| -5 | 119 | -80 |
| -3 | 6* | -17 |
| -1 | 97 | -82 |
| 1 | 110 | -117 |
| 3 | 45 | -48 |
| 5 | 90 | -87 |
| 7 | 106 | -51 |
| 9 | 7* | -7 |
| 11 | 8* | 8 |
| 13 | 28 | -26 |
| 15 | 19 | -23 |
| H, | K=4 | L=1 |
| -14 | 11* | -19 |
| -12 | 35 | -31 |
| -8 | 35 | -28 |
| -6 | 176 | -182 |
| -4 | 195 | -193 |
| -2 | 101 | 94 |
| 0 | 123 | 130 |
| 2 | 196 | -230 |
| 4 | 266 | -252 |
| 6 | 64 | -49 |
| 8 | 45 | 31 |
| 10 | 30 | -26 |
| 12 | 39 | -30 |
| 14 | 7* | -7 |
| H, | K=5 | L=1 |
| -13 | 33 | -26 |
| -9 | 44 | 41 |
| -7 | 116 | -113 |
| -5 | 254 | -263 |
| -1 | 173 | 150 |
| 1 | 7* | -16 |
| 3 | 240 | -262 |
| 5 | 122 | -129 |
| 7 | 69 | 62 |
| 11 | 60 | -49 |
| 13 | 11* | -16 |
| H, | K=6 | L=1 |
| -12 | 19* | -12 |
| -6 | 110 | -103 |
| -4 | 126 | -117 |
| -2 | 79 | 49 |
| 0 | 63 | 49 |
| 2 | 110 | -119 |
| 4 | 115 | -118 |
| 6 | 21 | -19 |
| 10 | 12* | -10 |
| 12 | 12* | -13 |
| H, | K=7 | L=1 |
| -13 | 14* | 18 |
| -9 | 82 | -75 |
| -7 | 46 | -49 |
| -5 | 54 | 51 |
| -3 | 18 | 6 |
| -1 | 107 | -102 |
| 1 | 48 | -40 |
| 3 | 23 | 22 |
| 5 | 58 | -54 |
| 7 | 84 | -81 |
| 9 | 6* | -5 |
| 11 | 31 | 31 |
| 15 | 12* | -19 |
| H, | K=8 | L=1 |
| -16 | 3* | -20 |
| -14 | 13* | 18 |
| -12 | 45 | 48 |
| -10 | 39 | -45 |
| -8 | 97 | -95 |
| -6 | 37 | 31 |
| -4 | 75 | 76 |
| -2 | 101 | -100 |
| 0 | 94 | -101 |
| 2 | 79 | 84 |
| 4 | 58 | 59 |
| 6 | 93 | -86 |
| 8 | 57 | -57 |
| 10 | 45 | 40 |
| 12 | 26 | 24 |
| H, | K=9 | L=1 |
| -13 | 22 | 24 |
| -11 | 8* | 16 |
| -9 | 26 | -23 |
| -7 | 8* | -9 |
| -5 | 55 | 51 |
| -3 | 39 | 35 |
| -1 | 42 | -38 |
| 3 | 77 | 78 |
| 7 | 41 | -44 |
| 11 | 37 | 34 |
| H, | K=10 | L=1 |
| -14 | 8* | -9 |
| -10 | 29 | 29 |
| -8 | 57 | 44 |
| -6 | 23 | 30 |
| -4 | 25 | 29 |
| -2 | 53 | 54 |
| 0 | 59 | 67 |
| 2 | 15* | 14 |
| 6 | 48 | 52 |
| 8 | 46 | 47 |
| H, | K=11 | L=1 |
| -13 | 13* | -23 |
| -9 | 84 | 89 |
| -7 | 68 | 67 |
| -5 | 38 | -40 |
| -1 | 109 | 119 |
| 1 | 44 | 44 |
| 3 | 21 | -25 |
| 5 | 65 | 67 |
| 7 | 91 | 100 |
| 11 | 33 | -34 |
| H, | K=12 | L=1 |
| -12 | 14* | -21 |
| -10 | 21 | 23 |
| -8 | 71 | 72 |
| -6 | 8* | 20 |
| -4 | 8* | -14 |
| -2 | 40 | 50 |
| 0 | 53 | 55 |
| 4 | 27 | 29 |
| 6 | 66 | 71 |
| 8 | 25 | 25 |
| 10 | 12* | -22 |
| H, | K=13 | L=1 |
| -11 | 9* | -13 |
| -7 | 61 | 47 |
| -5 | 64 | 66 |
| -1 | 19* | -24 |
| 1 | 12* | 15 |
| 3 | 47 | 45 |
| 5 | 36 | 39 |
| 9 | 10* | -13 |
| H, | K=14 | L=1 |
| -10 | 8* | -15 |
| -6 | 61 | 66 |
| -4 | 46 | 60 |
| -2 | 46 | -52 |
| 0 | 62 | -72 |
| 2 | 59 | 64 |
| 4 | 95 | 106 |
| 8 | 33 | -33 |
| H, | K=15 | L=1 |
| -9 | 8* | -14 |
| -7 | 14* | 25 |
| -5 | 63 | 68 |
| -1 | 57 | -65 |
| 3 | 84 | 78 |
| 5 | 28 | 31 |
| 7 | 6* | -18 |
| H, | K=16 | L=1 |
| -4 | 10* | 15 |
| 4 | 16* | 5 |
| H, | K=17 | L=1 |
| -5 | 32 | -38 |
| -1 | 27 | 27 |
| H, | K=18 | L=1 |
| 0 | 8* | 15 |
| 2 | 12* | -26 |
| H, | K=0 | L=2 |
| -16 | 23 | -21 |
| -12 | 47 | -45 |
| -10 | 133 | -127 |
| -8 | 37 | -35 |
| -6 | 98 | 85 |
| -4 | 139 | -153 |
| -2 | 104R | -431 |
| 0 | 174 | -199 |
| 2 | 152 | 165 |
| 4 | 66 | 51 |
| 6 | 188 | -205 |
| 8 | 145 | -146 |
| H, | K=1 | L=2 |
| -17 | 17 | -11 |
| -15 | 24 | -20 |
| -13 | 24 | -26 |
| -11 | 67 | -59 |
| -9 | 68 | -63 |
| -7 | 43 | 37 |
| -5 | 33 | 23 |
| -3 | 77R | -262 |
| -1 | 74R | -308 |
| 1 | 22 | 15 |
| 3 | 67 | 59 |
| 5 | 113 | -107 |
| 7 | 105 | -108 |
| 9 | 27 | -32 |
| 11 | 9* | -15 |
| H, | K=2 | L=2 |
| -14 | 40 | -38 |
| -12 | 36 | -33 |
| -10 | 34 | 29 |
| -8 | 5* | 16 |
| -6 | 96 | -80 |
| -4 | 64 | -62 |
| -2 | 6* | -2 |
| 0 | 79 | -83 |
| 2 | 105 | -104 |
| 4 | 15 | -8 |
| 6 | 25 | 19 |
| 8 | 39 | -32 |
| 10 | 29 | -44 |
| H, | K=3 | L=2 |
| -15 | 8* | -17 |
| -13 | 48 | -48 |
| -11 | 13* | 21 |
| -9 | 76 | 84 |
| -7 | 52 | -51 |
| -5 | 154 | -172 |
| -3 | 37 | 33 |
| -1 | 171 | 166 |
| 1 | 89 | -89 |
| 3 | 108 | -117 |
| 5 | 103 | 103 |
| 7 | 123R | 97 |
| 9 | 96 | -90 |
| 11 | 53 | -52 |
| 13 | 15* | 29 |
| H, | K=4 | L=2 |
| -14 | 37 | -40 |
| -12 | 23 | -24 |
| -10 | 73 | 71 |
| -8 | 45 | 40 |
| -6 | 85 | -66 |
| -4 | 22 | -21 |
| -2 | 85 | 80 |
| 0 | 39 | -20 |
| 2 | 96 | -90 |
| 6 | 84 | 80 |
| 10 | 54 | -56 |
| 14 | 13* | 28 |
| H, | K=5 | L=2 |
| -13 | 9* | 14 |
| -7 | 34 | 33 |
| -5 | 43 | 39 |
| 1 | 29 | 14 |
| 3 | 22 | 20 |
| 9 | 22 | 20 |
| 11 | 23 | 25 |
| H, | K=6 | L=2 |
| -14 | 60 | 60 |
| -12 | 46 | 42 |
| -10 | 62 | -63 |
| -8 | 31 | -31 |
| -6 | 117 | 126 |
| -4 | 77 | 80 |
| -2 | 39 | -48 |
| 0 | 73 | 69 |
| 2 | 147 | 170 |
| 4 | 5* | 18 |
| 6 | 95 | -77 |
| 8 | 24 | 26 |
| 10 | 80 | 80 |
| H, | K=7 | L=2 |
| -15 | 21 | 22 |
| -13 | 56 | 55 |
| -11 | 9* | 14 |
| -9 | 43 | -40 |
| -7 | 50 | 46 |
| -5 | 161 | 155 |
| -3 | 55 | 48 |
| -1 | 45 | -34 |
| 1 | 112 | 114 |
| 3 | 126 | 117 |
| 5 | 38 | -36 |
| 9 | 93 | 91 |
| 11 | 38 | 44 |
| 13 | 8* | -16 |
| H, | K=8 | L=2 |
| -14 | 33 | 22 |
| -12 | 26 | 35 |
| -10 | 9* | 12 |
| -8 | 6* | 8 |
| -6 | 33 | 34 |
| -4 | 59 | 58 |
| -2 | 96 | 98 |
| 0 | 80 | 80 |
| 6 | 55 | 50 |
| 8 | 69 | 59 |
| 10 | 26 | 32 |
| H, | K=9 | L=2 |
| -11 | 54 | 49 |
| -9 | 35 | 33 |
| -7 | 79 | -79 |
| -5 | 55 | -50 |
| -3 | 157 | 160 |
| -1 | 177 | 178 |
| 1 | 31 | -26 |
| 3 | 84 | -81 |
| 5 | 40 | 39 |
| 7 | 88 | 78 |
| 9 | 13* | 16 |
| H, | K=10 | L=2 |
| -12 | 8* | 14 |
| -10 | 50 | 49 |
| -6 | 68 | -73 |
| -4 | 37 | 33 |
| -2 | 174 | 178 |
| 0 | 73 | 65 |
| 2 | 102 | -106 |
| 4 | 34 | -36 |
| 6 | 98 | 88 |
| 8 | 55 | 52 |
| 12 | 7* | 2 |
| H, | K=11 | L=2 |
| -9 | 5* | 15 |
| -7 | 7* | 8 |
| -3 | 58 | 55 |
| -1 | 67 | 63 |
| 5 | 42 | 34 |
| 7 | 33 | 30 |
| 11 | 7* | 16 |
| H, | K=12 | L=2 |
| -12 | 4* | 16 |
| -10 | 25 | -26 |
| -8 | 6* | -18 |
| -6 | 56 | 50 |
| -4 | 34 | 35 |
| -2 | 36 | -27 |
| 0 | 6* | 14 |
| 2 | 85 | 81 |
| 4 | 7* | 10 |
| 6 | 43 | -42 |
| 8 | 9* | 5 |
| 10 | 30 | 31 |
| H, | K=13 | L=2 |
| -11 | 9* | -16 |
| -9 | 43 | -43 |
| -7 | 13* | 19 |
| -5 | 53 | 49 |
| -3 | 33 | -34 |
| -1 | 54 | -55 |
| 1 | 33 | 34 |
| 3 | 34 | 36 |
| 5 | 45 | -46 |
| 7 | 33 | -36 |
| 9 | 26 | 28 |
| 11 | 7* | 23 |
| H, | K=14 | L=2 |
| -10 | 11* | -20 |
| -8 | 11* | -18 |
| -2 | 42 | -46 |
| 0 | 26 | -28 |
| 4 | 21* | -19 |
| 6 | 27 | -25 |
| H, | K=15 | L=2 |
| -7 | 26 | -31 |
| -5 | 43 | -44 |
| -3 | 6* | -14 |
| 1 | 26 | -28 |
| 3 | 26 | -28 |
| H, | K=16 | L=2 |
| -6 | 39 | -45 |
| -4 | 39 | -41 |
| 0 | 12* | -16 |
| 2 | 56 | -56 |
| 4 | 15* | -3 |
| 6 | 14* | 23 |
| H, | K=17 | L=2 |
| -5 | 25 | -27 |
| -3 | 19 | -23 |
| -1 | 7* | -15 |
| 1 | 23 | -26 |
| 3 | 11* | -13 |
| H, | K=18 | L=2 |
| -4 | 16 | -18 |
| -2 | 37 | -45 |
| 0 | 18 | -22 |
| H, | K=1 | L=3 |
| -15 | 35 | -35 |
| -13 | 55 | -31 |
| -11 | 64 | 58 |
| -9 | 58 | 53 |
| -7 | 87 | -51 |
| -5 | 53 | -48 |
| -3 | 123 | 142 |
| -1 | 40 | 44 |
| 1 | 103 | -115 |
| 5 | 93 | 97 |
| 9 | 66 | -69 |
| H, | K=2 | L=3 |
| -16 | 7* | -16 |
| -14 | 42 | -43 |
| -12 | 42 | 39 |
| -10 | 110 | 116 |
| -6 | 95 | -95 |
| -4 | 47 | 47 |
| -2 | 115 | 139 |
| 0 | 39 | -31 |
| 2 | 68 | -64 |
| 4 | 120 | 132 |
| 6 | 111 | 114 |
| 8 | 60 | -54 |
| 10 | 41 | -44 |
| 12 | 39 | 39 |
| H, | K=3 | L=3 |
| -11 | 43 | 46 |
| -9 | 79 | 80 |
| -7 | 50 | 49 |
| -5 | 36 | 27 |
| -3 | 59 | 53 |
| -1 | 83 | 69 |
| 1 | 83 | 87 |
| 3 | 93 | 98 |
| 5 | 70 | 62 |
| 11 | 39 | 23 |
| 13 | 15* | 25 |
| H, | K=4 | L=3 |
| -12 | 10* | -7 |
| -10 | 10* | 16 |
| -8 | 123 | 131 |
| -6 | 125 | 141 |
| -4 | 12* | -18 |
| -2 | 62 | -47 |
| 0 | 133 | 157 |
| 2 | 221 | 235 |
| 4 | 56 | 51 |
| 6 | 62 | -54 |
| 10 | 52 | 56 |
| 12 | 14* | 24 |
| H, | K=5 | L=3 |
| -13 | 14* | 20 |
| -9 | 56 | 50 |
| -7 | 178 | 159 |
| -5 | 61 | 59 |
| -3 | 158 | -208 |
| 1 | 273 | 301 |
| 3 | 141 | 142 |
| 5 | 64 | -57 |
| 9 | 54 | 49 |
| 11 | 10* | 22 |
| H, | K=6 | L=3 |
| -10 | 38 | 28 |
| -8 | 74 | 73 |
| -6 | 57 | 52 |
| -4 | 38 | -15 |
| -2 | 26 | -22 |
| 0 | 81 | 69 |
| 2 | 121 | 132 |
| 4 | 55 | 41 |
| 6 | 34 | -31 |
| 10 | 26 | 27 |
| H, | K=7 | L=3 |
| -15 | 7* | -18 |
| -11 | 44 | 44 |
| -9 | 37 | 32 |
| -7 | 10* | -19 |
| -3 | 84 | 79 |
| -1 | 67 | 63 |
| 5 | 66 | 62 |
| 7 | 10* | 18 |
| 9 | 31 | -29 |
| 13 | 10* | 30 |
| H, | K=8 | L=3 |
| -14 | 32 | -31 |
| -12 | 30 | 27 |
| -10 | 84 | 83 |
| -6 | 84 | -86 |
| -4 | 42 | 39 |
| -2 | 97 | 100 |
| 0 | 54 | -51 |
| 2 | 75 | -68 |
| 4 | 93 | 69 |
| 6 | 89 | 81 |
| 8 | 45 | -41 |
| 10 | 36 | -39 |
| 12 | 11* | 22 |
| H, | K=9 | L=3 |
| -13 | 22 | -18 |
| -11 | 14* | 22 |
| -9 | 10* | 22 |
| -7 | 57 | -54 |
| -5 | 46 | -40 |
| -3 | 49 | 44 |
| 1 | 74 | -69 |
| 5 | 48 | 36 |
| 7 | 7* | -18 |
| 9 | 31 | -33 |
| H, | K=10 | L=. |
| -12 | 26 | -24 |
| -10 | 60 | -56 |
| -8 | 10* | -21 |
| -4 | 50 | -39 |
| -2 | 62 | -54 |
| 2 | 14* | -20 |
| 4 | 79 | -68 |
| 6 | 50 | -47 |
| H, | K=11 | L=3 |
| -11 | 56 | -57 |
| -9 | 56 | -56 |
| -7 | 10* | 17 |
| -3 | 57 | -58 |
| -1 | 64 | -70 |
| 1 | 10* | 17 |
| 3 | 35 | -30 |
| 5 | 97 | -89 |
| 7 | 10* | -16 |
| 9 | 31 | 36 |
| H, | K=12 | L=3 |
| -10 | 55 | -59 |
| -8 | 32 | -23 |
| -6 | 10* | 20 |
| -4 | 40 | -32 |
| -2 | 68 | -67 |
| 0 | 10* | -12 |
| 4 | 68 | -64 |
| 6 | 37 | -34 |
| 10 | 12* | 1 |
| H, | K=13 | L=3 |
| -9 | 43 | -42 |
| -7 | 43 | -42 |
| -3 | 32 | 30 |
| 1 | 63 | -58 |
| 3 | 65 | -62 |
| 7 | 9* | 13 |
| H, | K=14 | L=3 |
| -8 | 49 | -52 |
| -6 | 57 | -55 |
| -4 | 42 | 40 |
| -2 | 58 | 57 |
| 0 | 64 | -61 |
| 2 | 90 | -52 |
| 6 | 35 | 36 |
| H, | K=15 | L=3 |
| -7 | 44 | -49 |
| -3 | 52 | 53 |
| 1 | 73 | -78 |
| 3 | 40 | -37 |
| 5 | 23 | 29 |
| H, | K=17 | L=3 |
| -3 | 22 | -20 |
| -1 | 25 | -7 |
| H, | K=0 | L=4 |
| -14 | 36 | 34 |
| -12 | 76 | 74 |
| -10 | 30 | 25 |
| -8 | 72 | -71 |
| -6 | 59 | 55 |
| -4 | 246 | 295 |
| -2 | 140 | 179 |
| 0 | 87 | -111 |
| 2 | 25 | -19 |
| 4 | 173 | 207 |
| 6 | 120 | 126 |
| H, | K=1 | L=4 |
| -17 | 5* | 17 |
| -13 | 34 | 27 |
| -11 | 33 | 43 |
| -5 | 147 | 162 |
| -3 | 175 | 211 |
| 1 | 77 | -81 |
| 3 | 57 | 69 |
| 5 | 131 | 135 |
| 7 | 63 | 57 |
| H, | K=2 | L=4 |
| -8 | 11* | 57 |
| -6 | 79 | 52 |
| -4 | 11* | 19 |
| -2 | 10* | 5 |
| 0 | 68 | 67 |
| 2 | 28 | 28 |
| 4 | 10* | -22 |
| 6 | 42 | 34 |
| 8 | 62 | 61 |
| H, | K=3 | L=4 |
| -11 | 77 | -78 |
| -9 | 21* | 23 |
| -7 | 111 | 113 |
| -5 | 48 | -38 |
| -3 | 97 | -93 |
| -1 | 89 | 90 |
| 1 | 109 | 115 |
| 3 | 51 | -45 |
| 5 | 61 | -62 |
| 7 | 56 | 50 |
| 9 | 47 | 53 |
| H, | K=4 | L=4 |
| -16 | 36 | 18 |
| -12 | 38 | -35 |
| -10 | 44 | -36 |
| -8 | 50 | 53 |
| -6 | 72 | 64 |
| -4 | 56 | -61 |
| -2 | 61 | -49 |
| 0 | 90 | 88 |
| 2 | 13* | 15 |
| 4 | 54 | -55 |
| 6 | 65 | 65 |
| H, | K=5 | L=4 |
| -7 | 28 | -20 |
| -1 | 32 | -25 |
| 1 | 54 | -46 |
| H, | K=6 | L=4 |
| -16 | 14 | -31 |
| -14 | 17* | -26 |
| -12 | 40 | 41 |
| -10 | 35 | 29 |
| -8 | 101 | -101 |
| -6 | 114 | -107 |
| -4 | 35 | 38 |
| 0 | 122 | -123 |
| 2 | 33 | -35 |
| 4 | 82 | 74 |
| 6 | 17* | -24 |
| 8 | 57 | -57 |
| 10 | 16* | -23 |
| H, | K=7 | L=4 |
| -15 | 36 | -46 |
| -11 | 42 | 43 |
| -9 | 39 | -33 |
| -7 | 114 | -114 |
| -5 | 33 | -30 |
| -3 | 11* | 10 |
| -1 | 91 | -67 |
| 1 | 55 | -51 |
| 7 | 76 | -68 |
| 9 | 52 | -50 |
| H, | K=8 | L=4 |
| -14 | 23 | -26 |
| -6 | 80 | -69 |
| -4 | 85 | -80 |
| -2 | 40 | -40 |
| 0 | 33 | -32 |
| 2 | 20* | -20 |
| 4 | 21* | -26 |
| 6 | 68 | -59 |
| 8 | 46 | -37 |
| H, | K=9 | L=4 |
| -13 | 23 | -17 |
| -11 | 16* | -23 |
| -9 | 27* | 25 |
| -7 | 28* | 30 |
| -5 | 114 | -106 |
| -3 | 167 | -162 |
| -1 | 34 | 22 |
| 1 | 129 | 117 |
| 3 | 17* | -31 |
| 5 | 126 | -105 |
| 7 | 33 | -26 |
| H, | K=10 | L=4 |
| -12 | 28 | -29 |
| -8 | 56 | 53 |
| -6 | 18* | -20 |
| -4 | 149 | -140 |
| -2 | 80 | -61 |
| 0 | 101 | 89 |
| 2 | 38 | 32 |
| 4 | 104 | -89 |
| 6 | 67 | -59 |
| H, | K=11 | L=4 |
| -5 | 46 | -45 |
| -3 | 60 | -49 |
| 3 | 32 | -26 |
| 5 | 25* | -33 |
| 7 | 11* | -15 |
| H, | K=12 | L=4 |
| -8 | 51 | -49 |
| -6 | 44 | -40 |
| -4 | 35 | 21 |
| 0 | 56 | -43 |
| 2 | 17* | -11 |
| 4 | 25* | 30 |
| 8 | 33 | -38 |
| H, | K=13 | L=4 |
| -7 | 54 | -45 |
| -3 | 71 | 59 |
| -1 | 30 | -23 |
| 1 | 52 | -45 |
| 3 | 40 | 37 |
| 5 | 44 | 41 |
| 7 | 32 | -26 |
| H, | K=14 | L=4 |
| -4 | 37 | 34 |
| -2 | 39 | 26 |
| 8 | 13 | 0 |
| H, | K=15 | L=4 |
| -1 | 34 | 27 |
| 1 | 41 | 42 |
| H, | K=16 | L=4 |
| 0 | 41 | 41 |
| H, | K=1 | L=5 |
| -15 | 14* | 22 |
| -13 | 47 | -47 |
| -11 | 46 | -50 |
| -9 | 44 | 50 |
| -7 | 41 | 42 |
| -5 | 64 | -75 |
| -3 | 38 | -38 |
| -1 | 71 | 81 |
| 1 | 7* | 16 |
| 3 | 85 | -57 |
| 5 | 19* | -30 |
| 7 | 56 | 60 |
| H, | K=2 | L=5 |
| -12 | 62 | -73 |
| -8 | 77 | 86 |
| -4 | 129 | -153 |
| -2 | 22 | -17 |
| 0 | 66 | 60 |
| 2 | 81 | -88 |
| 4 | 80 | -88 |
| 6 | 46 | 48 |
| 8 | 41 | 40 |
| 10 | 9* | -28 |
| H, | K=3 | L=5 |
| -13 | 18* | -38 |
| -11 | 31* | -56 |
| -7 | 9* | -15 |
| -5 | 40 | -37 |
| -3 | 55 | -54 |
| -1 | 79 | -74 |
| 1 | 77 | -81 |
| 3 | 46 | -51 |
| 9 | 13* | -27 |
| H, | K=4 | L=5 |
| -10 | 86 | -52 |
| -8 | 103 | -110 |
| -6 | 33 | 29 |
| -4 | 76 | 71 |
| -2 | 126 | -117 |
| 0 | 166 | -193 |
| 2 | 58 | -44 |
| 4 | 40 | 32 |
| 6 | 14* | -28 |
| 8 | 59 | -57 |
| 10 | 12* | -25 |
| H, | K=5 | L=5 |
| -11 | 19* | -26 |
| -9 | 102 | -106 |
| -7 | 47 | -46 |
| -5 | 92 | 94 |
| -1 | 202 | -212 |
| 1 | 160 | -158 |
| 3 | 52 | 60 |
| 5 | 61 | 58 |
| 7 | 52 | -56 |
| 9 | 46 | -45 |
| H, | K=6 | L=5 |
| -10 | 20* | -39 |
| -8 | 31* | -53 |
| -6 | 56 | 20 |
| -4 | 44 | 38 |
| -2 | 100 | -88 |
| 0 | 135 | -115 |
| 2 | 9* | -6 |
| 4 | 14* | 21 |
| 6 | 9* | -20 |
| H, | K=7 | L=5 |
| -13 | 34 | -37 |
| -11 | 52 | -48 |
| -9 | 72 | -56 |
| -3 | 53 | -38 |
| -1 | 33 | 30 |
| 1 | 9* | -15 |
| 3 | 84 | -68 |
| 5 | 10* | -21 |
| H, | K=8 | L=5 |
| -12 | 48 | -50 |
| -8 | 65 | 68 |
| -4 | 103 | -97 |
| 0 | 79 | 64 |
| 2 | 58 | -51 |
| 4 | 73 | -69 |
| 6 | 35 | 36 |
| 8 | 46 | 44 |
| H, | K=9 | L=5 |
| -9 | 27* | 35 |
| -7 | 37 | 31 |
| -5 | 10* | -25 |
| -1 | 59 | 45 |
| 1 | 30* | 21 |
| 3 | 35 | -27 |
| 7 | 37 | 37 |
| H, | K=10 | L=5 |
| -12 | 18* | 29 |
| -6 | 20* | 24 |
| -4 | 61 | 50 |
| -2 | 49 | 34 |
| 0 | 10* | 12 |
| 2 | 36 | 31 |
| 4 | 45 | 42 |
| H, | K=11 | L=5 |
| -11 | 29 | 55 |
| -5 | 71 | 72 |
| -3 | 64 | 56 |
| 1 | 27* | 23 |
| 3 | 90 | 83 |
| 5 | 21* | 24 |
| 7 | 19* | -24 |
| H, | K=12 | L=5 |
| -10 | 16* | 30 |
| -4 | 66 | 56 |
| -2 | 34 | 24 |
| 2 | 56 | 51 |
| 4 | 48 | 35 |
| 6 | 10* | -15 |
| H, | K=13 | L=5 |
| -9 | 15* | 21 |
| -5 | 8* | -17 |
| -3 | 9* | 7 |
| -1 | 72 | 61 |
| 1 | 61 | 51 |
| H, | K=14 | L=5 |
| -8 | 11* | 41 |
| -6 | 32 | -30 |
| -4 | 51 | -49 |
| -2 | 45 | 38 |
| 0 | 86 | 82 |
| 2 | 7* | 14 |
| 4 | 37 | -35 |
| H, | K=15 | L=5 |
| -5 | 31 | -40 |
| -1 | 57 | 65 |
| 1 | 44 | 41 |
| 3 | 7* | -23 |
| H, | K=0 | L=6 |
| -14 | 17* | -32 |
| -12 | 19* | -28 |
| -10 | 48 | 43 |
| -8 | 43 | -31 |
| -6 | 195 | -225 |
| -4 | 124 | -135 |
| -2 | 86 | 109 |
| 0 | 34 | 38 |
| 2 | 124 | -152 |
| 4 | 110 | -114 |
| H, | K=1 | L=6 |
| -9 | 34* | -7 |
| -7 | 88 | -87 |
| -5 | 106 | -125 |
| -3 | 31 | -22 |
| 1 | 41 | -44 |
| 3 | 116 | -132 |
| 5 | 51 | -55 |
| H, | K=2 | L=6 |
| -8 | 58 | -57 |
| -4 | 23* | -1 |
| -2 | 42 | -34 |
| 0 | 36 | -35 |
| 4 | 23* | -26 |
| 6 | 39 | -45 |
| H, | K=3 | L=6 |
| -13 | 50 | 56 |
| -9 | 84 | -51 |
| -7 | 23* | -23 |
| -5 | 80 | 73 |
| -3 | 39 | -29 |
| -1 | 112 | -104 |
| 1 | 52 | 35 |
| 3 | 74 | 81 |
| 5 | 28* | -48 |
| 7 | 46 | -67 |
| H, | K=4 | L=6 |
| -12 | 36 | 29 |
| -10 | 45 | -40 |
| -8 | 55 | -42 |
| -6 | 64 | 56 |
| -4 | 51 | 34 |
| -2 | 76 | -62 |
| 0 | 25* | -20 |
| 2 | 57 | 50 |
| 6 | 35* | -45 |
| H, | K=5 | L=6 |
| -7 | 29* | 9 |
| -3 | 27* | 23 |
| -1 | 31* | 19 |
| H, | K=6 | L=6 |
| -10 | 54 | 57 |
| -8 | 79 | 72 |
| -6 | 52 | -31 |
| -4 | 37* | -28 |
| -2 | 105 | 87 |
| 0 | 75 | 63 |
| 2 | 29* | -33 |
| 6 | 52 | 74 |
| H, | K=7 | L=6 |
| -9 | 79 | 87 |
| -7 | 53 | 50 |
| -3 | 55 | 42 |
| -1 | 106 | 89 |
| 3 | 12* | -15 |
| 5 | 59 | 66 |
| 7 | 43 | 55 |
| H, | K=8 | L=6 |
| -8 | 67 | 51 |
| -6 | 76 | 68 |
| -4 | 56 | 45 |
| 2 | 46 | 37 |
| 4 | 58 | 54 |
| 6 | 15* | 28 |
| H, | K=9 | L=6 |
| -9 | 14* | -23 |
| -7 | 71 | 64 |
| -5 | 114 | 101 |
| -1 | 92 | -73 |
| 1 | 34* | 26 |
| 3 | 112 | 99 |
| 5 | 41 | 39 |
| H, | K=10 | L=6 |
| -10 | 11* | -29 |
| -6 | 108 | 107 |
| -4 | 69 | 58 |
| -2 | 84 | -76 |
| 0 | 58 | -37 |
| 2 | 110 | 80 |
| 4 | 48 | 58 |
| H, | K=11 | L=6 |
| -7 | 40 | 36 |
| -5 | 42 | 35 |
| -3 | 15* | 6 |
| 3 | 38 | 35 |
| H, | K=12 | L=6 |
| -8 | 15* | 26 |
| -2 | 35 | 30 |
| 0 | 40 | 31 |
| 2 | 33 | -16 |
| H, | K=13 | L=6 |
| -5 | 46 | -46 |
| -1 | 32 | 28 |
| 1 | 17* | -24 |
| 3 | 25 | -41 |

[a] $h$, $F_o$, and $F_c$ are given for constant $k$ and $l$. An asterisk indicates visually estimated reflection (slightly above film background). R signifies rejected reflection (extinction or bad spot on photograph). Zero-observed reflections are not given, they all have $F_c$ below the minimum observable value.

pound. The results are: $a = 13.85 \pm 0.03$, $b = 14.94 \pm 0.03$, $c = 7.41 \pm 0.02$ Å, $\beta = 98.8 \pm 0.3°$, $V = 1515 \pm 7$ Å$^3$, $Z = 4$. The 94 nonzero observed $hk0$ reflections were used to refine the projection by Fourier and least-squares methods until $R = 0.09$. Under the influence of X-rays the crystal went over into a single crystal of space group $P2_1/c$, which presently is being studied.

## Results and Discussion

**Description of the Crystal Structure of $CuBr_2$(dtc).**—The atomic parameters are given in Table I. The structure is illustrated in Figure 1. Bond distances and angles[13] are given in Figure 2. The observed and calculated structure amplitudes are given in Table II. The molecule is situated on a twofold axis and, apart from the butyl chains, is planar within the accuracy of the structure determination. In the direction of the needle axis $c$ the molecules are piled on top of each other, adjacent molecules related by a center of symmetry.

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(13) Using "An Interatomic Distances and Angles Program" by R. Shiono and S. S. C. Chu.

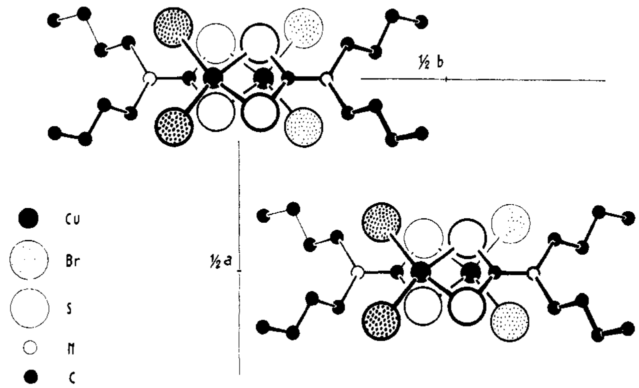

Figure 1.—Projection of $CuBr_2(dtc)$ along *c*. The molecules are situated on a twofold axis at $z = \pm^1/_4$.

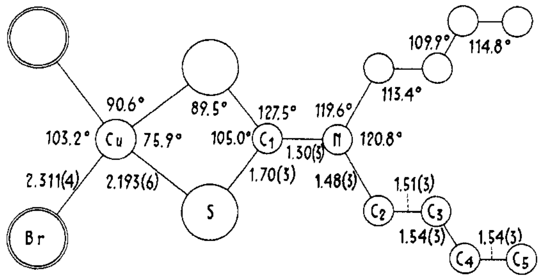

Figure 2.—Bond angles and distances in $CuBr_2(dtc)$. Projection on the plane through the flat part of the molecule. The Cu, C(1), and N atoms are situated on a twofold axis. Standard deviations of the bond distances (Å) are given in parentheses. The accuracy of the bond angles is limited to 0.3° by the inaccuracy of the monoclinic angle.

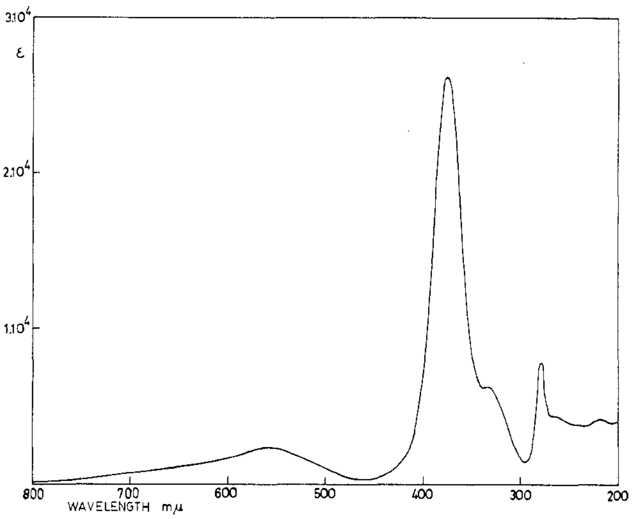

Figure 3.—Ultraviolet spectrum of $CuBr_2(dtc)$ in methylene chloride.

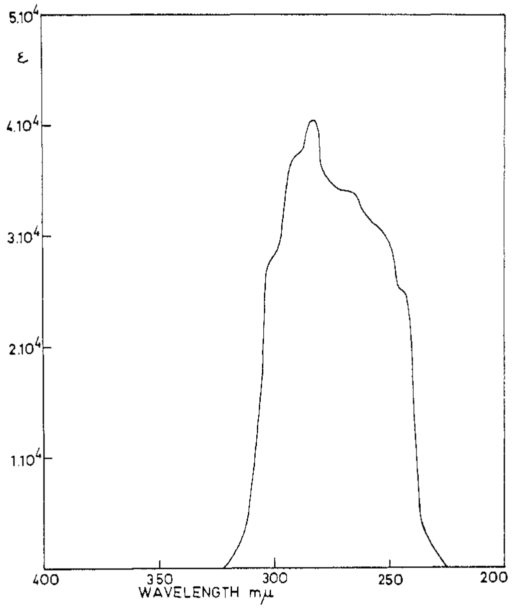

Figure 4.—Ultraviolet spectrum of $AuBr_2(dtc)$ in methylene chloride.

Bond lengths and bond angles in the dtc ligand agree very well with those in other dithiocarbamato complexes.[14] The Cu-S distance of 2.19 Å is close to the mean value of 2.17 Å in the bis(maleonitriledithiolato)-copper(III) ion.[7] However it is significantly shorter than the Cu(II)-S distance of 2.30 Å in $Cu(dtc)_2$.[15] The Cu-Br bond length of 2.31 Å also is short compared with those in Cu(II) compounds, *e.g.*, 2.54 Å in $\alpha$-$CuBr_2(NH_3)_2$,[16] 2.46 Å in $[CuBr_4(H_2O)_2]^{2-}$,[17] and 2.40 Å in $CuBr_2$.[18] These differences suggest that the metal-ligand bonds have an appreciable ionic contribution. Then the oxidation number of copper in these complexes could have more than formal significance, giving real information about the electronic configuration localized on the copper. Copper atoms are 4.07 Å apart; the shortest intermolecular Cu-S distance is 3.34 Å. This is an interesting difference with $Cu(dtc)_2$ where Cu has fivefold coordination, the fifth Cu-S distance, bridging two $Cu(dtc)_2$ units, being 2.85 Å.[12]

The two-dimensional analysis of $AuBr_2(dtc)$ has revealed a structure similar to $CuBr_2(dtc)$, only the butyl carbons being slightly displaced.

**Magnetic Properties.**—Molar magnetic susceptibilities (cgsu $mol^{-1}$) at room temperature for solid $CuBr_2(dtc)$ were found to be $\chi = -124 \times 10^{-6}$ and for solid $AuBr_2(dtc)$ $\chi = -247 \times 10^{-6}$. After correction for diamagnetism the effective magnetic moments can be calculated to be 0.5 and 0.0 BM, respectively. These results agree with a low-spin $d^8$ configuration which is the normal situation in other $d^8$ ions in planar fourfold coordination. The value of 0.5 BM for $CuBr_2(dtc)$ could be due to temperature-independent paramagnetism.

**Spectra.**—In the infrared spectra of $CuBr_2(dtc)$ and Cu(dtc) the C-N stretching frequencies are at 1560 and 1475 $cm^{-1}$, respectively. This agrees with the expected difference in bond order in these compounds. A similar shift in C-N stretching frequency is observed in the series $AuBr_2(dtc)$, $Au(dtc)_2AuBr_2$, and $Au(dtc)$.[1,8] Ultraviolet spectra of $CuBr_2(dtc)$ and $AuBr_2(dtc)$ are illustrated in Figures 3 and 4. At present no interpretation of these spectra is available.

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