Lewis Base Adducts of Group 11 Metal(I) Complexes. Part 48.[1] Heterobimetallic Tris(dithiocarbamato)cobalt(III)–Copper(I) Halide Adducts as a Vehicle for Novel Copper(I) Halide Clusters (Structurally Characterized) *

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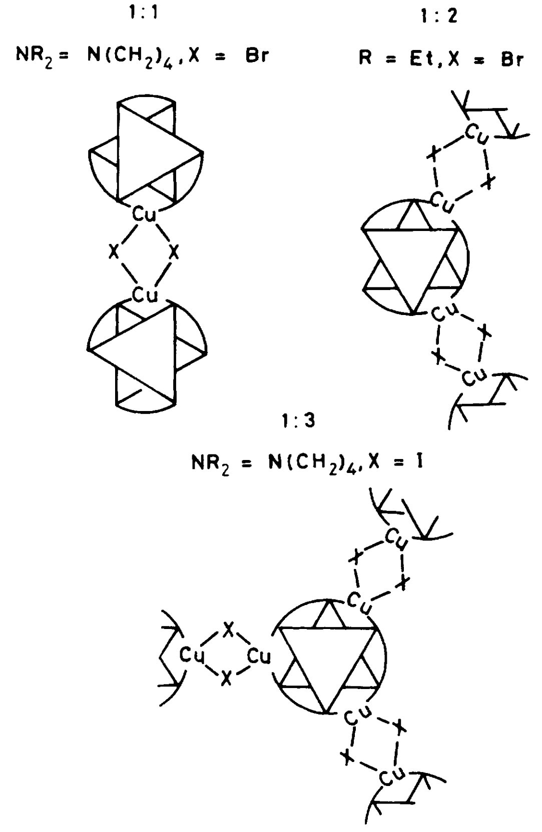
Reaction of tris(*N,N*-disubstituted dithiocarbamato)cobalt(III) complexes, $[Co(S_2CNR_2)_3]$, with copper(I) halides, CuX, in acetonitrile deposits 1 : 3 and 2 : 5 adducts, $[Co\{S_2CN(CH_2)_4\}_3]\cdot3CuBr\cdot MeCN$ (**1**) and $2[Co(S_2CNBu^n_2)_3]\cdot5CuI$ (**2**), characterized by single-crystal structure determination and shown to contain novel CuX aggregates. In (**1**), $[Co(S_2CNR_2)_3]$ molecules are linked by co-ordination of Cu_3Br_3 oligomers in two of the three interligand 'chelate' sites to yield a one-dimensional polymer. The Cu_3Br_3 unit is a six-membered ring in pseudo-'boat' conformation; two of the copper atoms are 'chelated' by $[Co(S_2CNR_2)_3]$ molecules, while the third is three-co-ordinate with an acetonitrile appended. In (**2**), $[Co(S_2CNR_2)_3]$ molecules are linked into a 1 : 1 dimer by chelated CuI_2Cu units; these units are further linked and cross-linked into a novel infinite double-stranded polymer by centrosymmetric Cu_6I_6 'displaced step' units.

In previous reports[2,3] we have shown how, in favourable circumstances by slow interdiffusion, crystals of the heterobimetallic adducts formed between tris(*N,N*-disubstituted dithiocarbamato)cobalt(III), $[Co(S_2CNR_2)_3]$, and copper(I) halides, CuX, may be obtained and characterized by single-crystal *X*-ray methods. Dimeric CuX_2Cu units may be 'chelated' between the upper and lower S_3 planes of the cobalt environment by the co-ordinately unsaturated sulphur atoms. In this manner, depending on whether one, two, or all three of these co-ordination sites are employed, examples of each of 1:1, 1:2, and 1:3 $[Co(S_2CNR_2)_3]$:CuX stoicheiometry have been obtained as dimeric, one-dimensional, or three-dimensional polymers respectively.



More recently, however, we have found that further novel stoicheiometries may be achieved by variation in the oligomeric nature of the copper halide bridging moiety. Here we show that the 1 : 3 stoicheiometry may also be achieved in a linear polymer form by use of a cyclic Cu_3I_3 bridging unit, the present representative being $[Co\{S_2CN(CH_2)_4\}_3]\cdot3CuBr\cdot MeCN$, (**1**); an even more unusual 2:5 species is obtained in $2[Co(S_2CNBu^n_2)_3]\cdot5CuI$, (**2**), in which 'displaced step' Cu_6I_6 bridges are found. The synthesis and structural characterization of both is described.

Experimental

Crystals of both derivatives were prepared by the same general techniques, the slow interdiffusion of layered, very dilute solutions of the copper(I) halide with the parent cobalt(III) dithiocarbamate complex. For complex (**1**) this reaction was carried out in a Schlenk apparatus under argon with acetonitrile solutions to give well formed black crystals (Found: C, 21.5; H, 2.9; N, 5.7. Calc. for $C_{17}H_{27}Br_3CoCu_3N_4S_6$: C, 21.1; H, 2.8; N, 5.8%). For (**2**) the reaction was carried out under ambient conditions with CuI dissolved in acetonitrile and the dithiocarbamate complex in dichloromethane, to give a very few small well formed crystals on evaporation of the solvent to dryness, together with unreacted CuI. The crystals decomposed without melting at 200—300 °C and are air-stable for a period of days.

Structure Determinations.—Unique data sets were measured at *ca.* 295 K using four-circle diffractometers in conventional 2θ—θ scan mode [monochromatic Mo-K_α radiation sources (λ 0.7106_9 Å)]. Within the specified $2\theta_{max.}$ limit, *N* independent reflections were obtained (no decomposition), N_o with $I > 3\sigma(I)$ being considered 'observed' and used in the large-block least-squares refinement after gaussian absorption correction and

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* *Supplementary data available:* see Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1989, Issue 1, pp. xvii—xx.

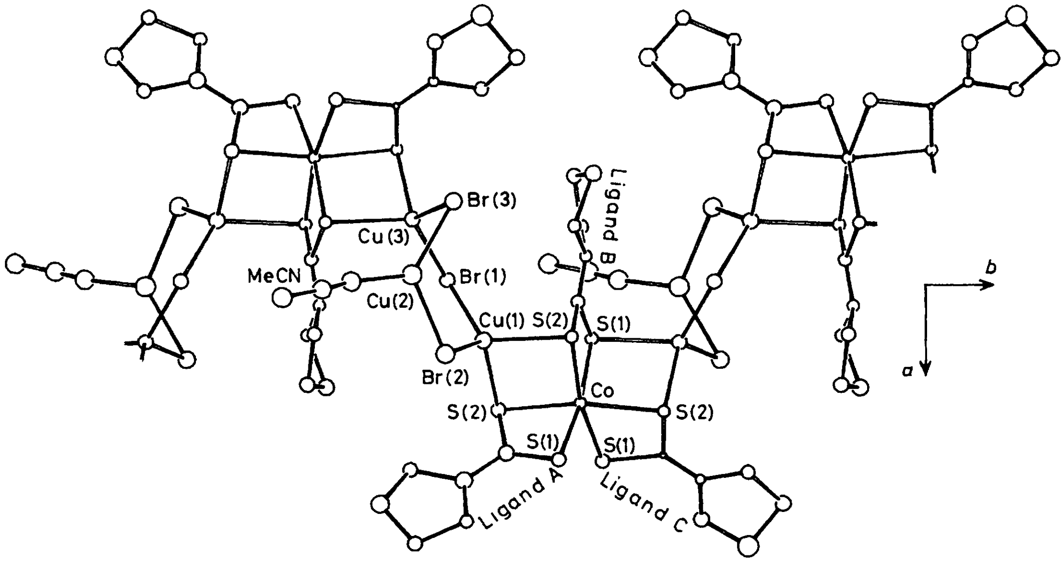


Figure 1. The polymer of complex (**1**) viewed down *c*; note the position of the origin located near Br(1); 20% thermal envelopes and labelling of the asymmetric unit are shown. Note the pseudo-boat conformation of the Cu_3Br_3 ring

solution of the structure by a combination of vector and direct methods. Anisotropic thermal parameters were refined for the non-hydrogen atoms; $(x, y, z, U_{iso.})_H$ were included at estimated values. Conventional residuals on $|F|$ at convergence, R, R', are quoted; statistical weights were used, derived from $\sigma^2(I) = \sigma^2(I_{diff.}) + 0.000n\sigma^4(I_{diff.})$. Neutral atom complex scattering factors were employed;[4] computation used the XTAL 83 program system[5] implemented by S. R. Hall on a Perkin-Elmer 3240 computer. Pertinent results are given in Tables 1—5 and Figures 1 and 2.

Crystal data. (**1**), $[Co\{S_2CN(CH_2)_4\}_3]\cdot 3CuBr\cdot MeCN$, $C_{17}H_{27}Br_3CoCu_3N_4S_6$, $M = 969.1$, orthorhombic, space group $P2_12_12_1(D_2{}^4$, no. 19), $a = 17.824(7)$, $b = 14.478(4)$, $c = 11.518(3)$ Å, $U = 2\,972(2)$ Å^3, $Z = 4$, $D_c = 2.17$ g cm^{-3}, $F(000) = 1\,888$, $\mu_{Mo} = 70$ cm^{-1}, specimen 0.10 × 0.15 × 0.31 mm, $A^*_{min.,max.}$ 1.67, 4.36, $2\theta_{max.} = 50°$, $N = 3\,776$, $N_o = 1\,238$, $R = 0.055$, $R'(n = 2) = 0.044$ (both chiralities). Syntex diffractometer.

(**2**), $2[Co(S_2CNBu^n{}_2)_3]\cdot 5CuI$, $C_{54}H_{108}Co_2Cu_5I_5N_6S_{12}$, $M = 2\,296.4$, triclinic, space group $P\bar{1}(C_i{}^1$, no. 2), $a = 20.800(9)$, $b = 16.752(8)$, $c = 13.563(6)$ Å, $\alpha = 110.65(3)$, $\beta = 94.01(3)$, $\gamma = 102.08(4)°$, $U = 4\,271(3)$ Å^3, $Z = 2$, $D_c = 1.79$ g cm^{-3}, $F(000) = 2\,260$, $\mu_{Mo} = 35.7$ cm^{-1}, specimen 0.17 × 0.15 × 0.10 mm, $A^*_{min.,max.} = 1.33$, 1.62, $2\theta_{max.} = 45°$, $N = 10\,067$, $N_o = 7\,433$, $R = 0.038$, $R'(n = 6) = 0.044$, Enraf–Nonius diffractometer.

Abnormal features. For complex (**1**) the data were limited in scope and C, N thermal parameters were refined with the isotropic form. For (**2**) one of the n-butyl substituents is disordered. Data collection terminated at $h \sim 16$ (*ca.* 90% of total) due to machine failure.

Additional material available from the Cambridge Crystallographic Data Centre comprises H-atom co-ordinates, thermal parameters, and remaining bond distances and angles.

Discussion

The results of the structure determinations are consistent with the stoicheiometries ascribed as above; in each case the asymmetric unit of the structure is the formula unit.

Complex (**1**).—It is of interest to compare the present compound with its iodide counterpart $[Co\{S_2CN(CH_2)_4\}_3]\cdot 3CuI$

Table 1. Non-hydrogen atom co-ordinates for complex (**1**)

Atom	*x*	*y*	*z*
Br(1)	−0.000 8(3)	0.000 3(3)	0.221 2(2)
Br(2)	0.113 5(2)	−0.003 5(3)	0.531 0(8)
Br(3)	−0.122 2(2)	0.011 4(3)	0.527 2(6)
Cu(1)	0.092 4(3)	0.067 9(4)	0.347 0(4)
Cu(2)	−0.009 3(3)	−0.066 1(3)	0.565 3(4)
N	0.001 3(17)	−0.179 8(18)	0.671 3(24)
C(1)	0.013 7(15)	−0.235 2(23)	0.738 3(37)
C(2)	0.026 1(18)	−0.310 2(23)	0.812 6(31)
Cu(3)	−0.094 9(3)	−0.065 3(4)	0.346 0(4)
Co	0.188 9(1)	0.249 8(6)	0.251 9(7)
Ligand A			
S(1)	0.199 3(5)	0.095 8(8)	0.225 0(9)
S(2)	0.276 0(5)	0.208 8(8)	0.386 5(10)
C(1)	0.266(2)	0.111(3)	0.336(4)
N	0.308(2)	0.031(3)	0.359(3)
C(2)	0.292(2)	−0.069(4)	0.321(3)
C(3)	0.344(2)	−0.126(3)	0.396(4)
C(4)	0.405(2)	−0.060(2)	0.433(3)
C(5)	0.372(2)	0.036(2)	0.446(4)
Ligand B			
S(1)	0.089 7(5)	0.271 0(9)	0.130 2(10)
S(2)	0.086 8(5)	0.233 2(8)	0.372 6(10)
C(1)	0.033(1)	0.245(3)	0.254(4)
N	−0.038(1)	0.260(2)	0.244(3)
C(2)	−0.084(2)	0.238(3)	0.348(4)
C(3)	−0.165(2)	0.273(3)	0.309(4)
C(4)	−0.161(2)	0.237(3)	0.188(4)
C(5)	−0.083(2)	0.251(3)	0.140(4)
Ligand C			
S(1)	0.278 1(5)	0.290 9(8)	0.120 7(10)
S(2)	0.201 5(5)	0.405 4(6)	0.277 5(8)
C(1)	0.269(1)	0.404(2)	0.173(2)
N	0.306(1)	0.474(2)	0.137(2)
C(2)	0.367(2)	0.476(3)	0.054(4)
C(3)	0.409(2)	0.563(3)	0.081(4)
C(4)	0.343(2)	0.629(3)	0.109(4)
C(5)	0.295(2)	0.563(3)	0.185(3)

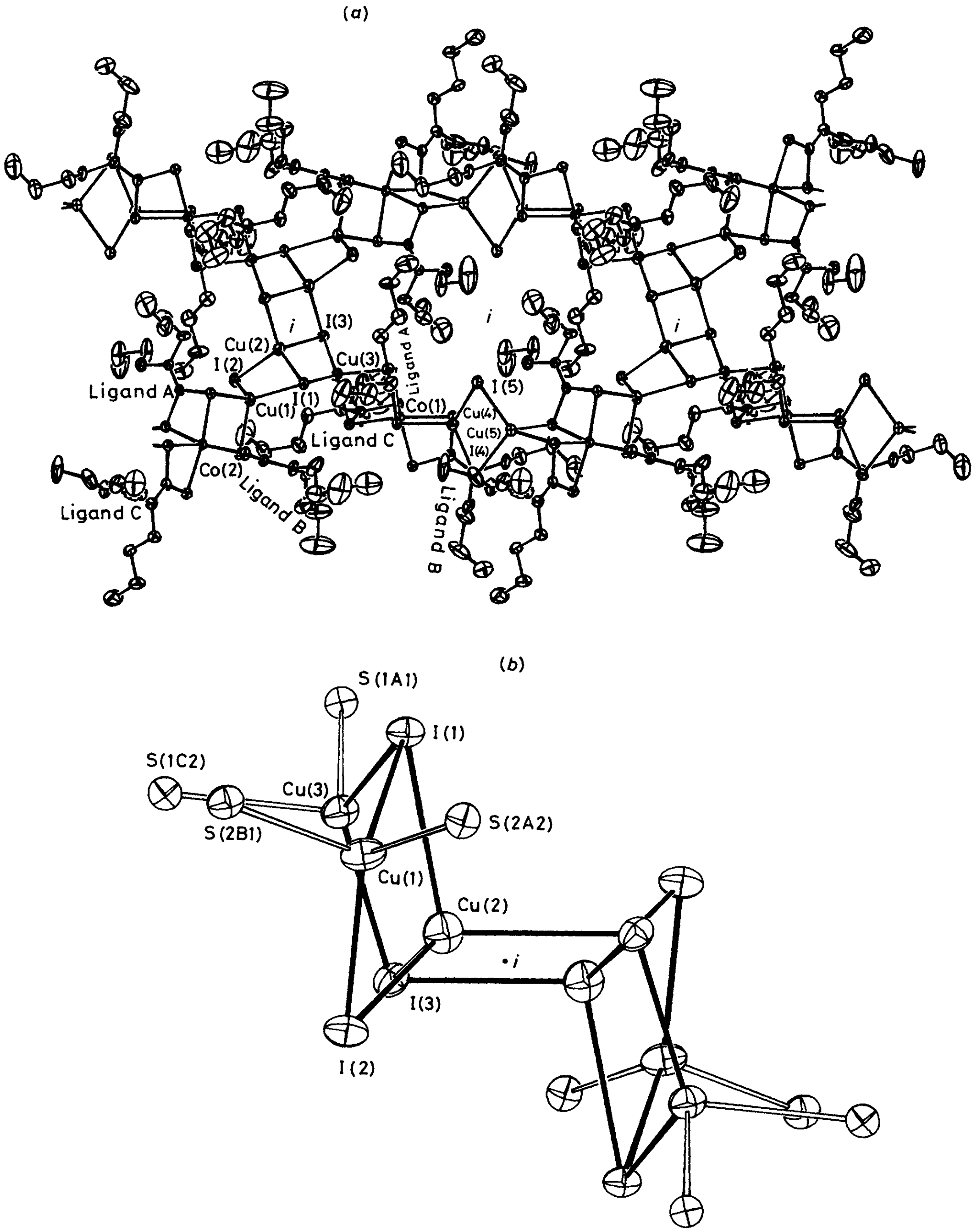


Figure 2. (*a*) The polymer of complex (**2**), showing fragment labelling. Note the linking of cobalt dithiocarbamate molecules by (*i*) Cu_2I_2 dimers, comprising Cu(4,5)I(4,5) and (*ii*) centrosymmetric Cu_6I_6 moieties. (*b*) The Cu_6I_6 oligomeric bridging unit

(unsolvated), recorded previously.[2] The latter is cubic and a network polymer created by the use of all interligand S · · · S sites for chelating of CuI_2Cu dimers, with consequent 1:3 stoicheiometry. In the present derivative, remarkably, only two of the S · · · S 'chelate' sites are utilized for chelation of copper, as in the derivative $[Co(S_2CNEt_2)_3]\cdot Cu_2Br_2\cdot 2MeCN$,[2] where the result is a one-dimensional polymeric array of $[Co(S_2CNEt_2)_3]$ units linked by $CuBr_2Cu$ dimers with the acetonitrile playing a solvating role only. In the present derivatives, however, the linking unit is a cyclic Cu_3Br_3 array with alternating copper and halogen atoms, *i.e.* 1:3 stoicheiometry is now achieved by variation of the degree of oligomerization of the copper(I) halide rather than by occupancy of an appropriate number of 'chelate' sites of the $[Co(S_2CNR_2)_3]$. Since, in this array, however, only two of the latter sites chelate copper atoms, one of the copper atoms of the Cu_3Br_3 ring has no sulphur interactions; instead, it is co-ordinated (co-ordination number three) by the acetonitrile molecule, now partaking of an active role in complex formation rather than passive occupancy of a co-ordination site. In complexes of the present type, where not all sulphur atoms interact with copper(I), ⟨Co–S⟩ (unchelated, 2.27 Å here) is usually 0.02—0.04 Å shorter than ⟨Co–S⟩ (chelated 2.28 Å here). Here the difference is only 0.01 Å, and the precision of the determination is such that its significance is

Table 2. Non-hydrogen atom co-ordinates for complex (**2**)

(*a*) Tris(*N*,*N*-di-n-butyldithiocarbamato)cobalt(III) species

Ligand *n*	A			B			C*		
Atom	*x*	*y*	*z*	*x*	*y*	*z*	*x*	*y*	*z*
Molecule 1									
Co(1)	0.215 79(5)	0.329 00(7)	0.499 93(8)						
S(1*n*1)	0.118 1(1)	0.301 3(1)	0.563 7(2)	0.215 7(1)	0.466 0(1)	0.501 8(2)	0.170 3(1)	0.262 9(2)	0.326 9(2)
S(1*n*2)	0.247 2(1)	0.380 8(1)	0.681 1(2)	0.317 5(1)	0.377 3(2)	0.465 1(2)	0.226 2(1)	0.187 2(1)	0.454 5(2)
C(1*n*1)	0.164 3(4)	0.348 8(5)	0.690 8(6)	0.294 8(5)	0.470 1(5)	0.467 6(7)	0.187 4(4)	0.168 8(5)	0.328 7(6)
N(1*n*)	0.139 9(4)	0.358 8(5)	0.778 7(5)	0.332 1(4)	0.534 7(5)	0.448 3(6)	0.172 4(4)	0.091 9(5)	0.247 3(6)
C(1*n*12)	0.067 9(6)	0.320 6(8)	0.775 6(8)	0.308 3(6)	0.613 6(6)	0.453 4(9)	0.133 2(7)	0.081 4(8)	0.145 9(9)
C(1*n*13)	0.033 4(7)	0.379 4(9)	0.847 0(11)	0.285 9(8)	0.612 3(9)	0.345 1(11)	0.173 3(8)	0.094 9(10)	0.068 9(11)
C(1*n*14)	−0.040 3(6)	0.333 9(10)	0.839 3(11)	0.265 2(9)	0.694 3(10)	0.350 8(13)	0.134 4(10)	0.110 5(13)	−0.023 2(11)
C(1*n*15)	−0.073 4(9)	0.393 0(13)	0.919 4(13)	0.318 9(14)	0.777 6(15)	0.396 9(21)	0.074 1(10)	0.057 2(15)	−0.074 9(12)
C(1*n*22)	0.181 9(6)	0.405 9(7)	0.883 4(7)	0.401 5(6)	0.534 5(7)	0.433 2(10)	0.188 2(6)	0.013 7(7)	0.257 4(8)
C(1*n*23)	0.186 6(7)	0.352 9(8)	0.948 6(9)	0.411 4(8)	0.497 2(12)	0.323 3(13)	0.246 4(8)	−0.007 4(11)	0.211 7(14)
C(1*n*24)	0.221 6(9)	0.410 9(10)	1.062 7(10)	0.486 3(10)	0.501 0(18)	0.321 0(20)	0.258 6(10)	−0.094 6(13)	0.211 9(18)
C(1*n*25)	0.225 7(12)	0.361 3(12)	1.132 5(13)	0.526 3(10)	0.568 2(16)	0.309 2(24)	0.214 2(17)	−0.174 4(15)	0.138 2(25)
Molecule 2									
Co(2)	0.298 19(6)	−0.085 49(7)	0.764 22(9)						
S(2*n*1)	0.248 4(1)	−0.226 0(1)	0.650 4(2)	0.306 7(1)	−0.023 0(1)	0.639 2(2)	0.404 3(1)	−0.097 7(2)	0.770 0(2)
S(2*n*2)	0.188 2(1)	−0.092 8(1)	0.761 7(2)	0.328 1(1)	0.061 1(2)	0.863 2(2)	0.313 3(1)	−0.130 7(2)	0.903 4(2)
C(2*n*1)	0.172 8(4)	−0.201 2(8)	0.677 3(7)	0.331 5(4)	0.076 4(5)	0.746 3(7)	0.395 0(4)	−0.120 8(5)	0.880 7(7)
N(2*n*)	0.114 0(3)	−0.255 6(4)	0.637 6(7)	0.347 7(4)	0.154 3(5)	0.735 9(6)	0.442 6(4)	−0.129 0(5)	0.943 0(6)
C(2*n*12)	0.106 8(5)	−0.349 1(6)	0.565 8(9)	0.349 5(5)	0.160 5(7)	0.632 5(8)	0.512 3(5)	−0.108 3(7)	0.926 6(8)
C(2*n*13)	0.066 7(10)	−0.375 5(8)	0.459 1(12)	0.415 4(7)	0.159 0(10)	0.598 2(11)	0.534 4(5)	−0.185 0(7)	0.861 1(9)
C(2*n*14)	0.065 8(10)	−0.469 2(9)	0.388 2(13)	0.417 6(9)	0.167 4(18)	0.494 9(16)	0.603 3(5)	−0.156 9(8)	0.832 9(9)
C(2*n*15)	0.069 2(24)	−0.491 6(20)	0.295 2(24)	0.487 0(13)	0.174 1(28)	0.461 1(21)	0.628 2(8)	−0.230 9(11)	0.769 0(15)
C(2*n*22)	0.053 9(5)	−0.225 9(8)	0.661 0(11)	0.353 5(8)	0.240 2(10)	0.834 3(12)	0.430 1(6)	−0.155 3(11)	1.033 6(10)
C(2*n*23)	0.020 4(8)	−0.263 7(12)	0.731 5(19)	0.417 0(9)	0.272 3(16)	0.874 0(19)	0.436 8(12)	−0.103 4(14)	1.127 4(20)
C(2*n*24)	0.051 4(10)	−0.221 8(13)	0.845 4(18)	0.418 0(18)	0.366 4(16)	0.995 5(19)	0.427 1(15)	−0.143 7(18)	1.218 2(20)
C(2*n*25)	0.011 9(17)	−0.257 8(21)	0.923 4(29)	0.403 0(13)	0.426 5(21)	0.957 4(21)	0.435 9(26)	−0.062 5(29)	1.331 5(26)

(*b*) Copper and iodine atoms

Atom	*x*	*y*	*z*
(*i*) Oligomer			
Cu(1)	0.187 92(6)	−0.031 81(7)	0.621 74(9)
Cu(2)	0.069 93(6)	−0.014 47(8)	0.521 23(10)
Cu(3)	0.126 54(6)	0.150 37(7)	0.525 54(8)
I(1)	0.162 19(3)	0.122 24(3)	0.693 09(4)
I(2)	0.128 76(3)	−0.137 68(4)	0.437 57(5)
I(3)	0.029 44(3)	0.048 39(4)	0.377 92(5)

Atom	*x*	*y*	*z*
(*ii*) Dimer			
Cu(4)	0.249 72(6)	0.529 80(7)	0.693 85(10)
Cu(5)	0.271 76(6)	0.710 26(7)	0.776 45(11)
I(4)	0.368 40(3)	0.631 63(4)	0.740 04(6)
I(5)	0.172 21(4)	0.608 21(4)	0.812 90(6)

* n-Butyl substituent 232 is disordered and was modelled in terms of equal occupancy (0.5) of two sets of sites for C(2323, 2324, 2325). Other components of these atoms are: C(2323′) 0.420(1), −0.230(1), 1.035(2); C(2324′) 0.408(2), −0.243(2), 1.138(2); C(2325′) 0.385(3), −0.339(2), 1.114(4).

slight. In the Cu_3Br_3 ring the geometries of the 'chelated' copper atom environments may be compared with those observed in $[Co(S_2CNEt_2)_3]\cdot Cu_2Br_2\cdot 2MeCN$. In that compound Br–Cu–Br was closed down relative to the present value by dimer formation, being 107.47(9) [*cf.* 117.8(3) and 118.4(3)°], while Cu–Br–Cu is 72.53(9) [*cf.* 106.4(2) (between the two chelated copper atoms) and 99.6(3) and 76.6(2)°]; Cu–Br were 2.451(4), 2.417(3) [av. 2.43$_4$ Å (*cf.* the present values of 2.387(10)—2.414(8) (av. 2.40$_4$ Å)] for chelated copper and 2.346(6) and 2.402(6) Å (av. 2.371 Å) for the unchelated copper. The Cu–S distances were 2.374(5) and 2.500(5) Å (av. 2.43$_7$ Å), *cf.* the present 2.39(1)—2.41(1) Å (av. 2.40 Å), *i.e.* curiously, in the present compound, in spite of the enlarged Br–Cu–Br angles with correspondingly shorter Cu–Br, Cu–S are also shorter by a considerable amount. The third copper atom, associated with the acetonitrile, is close to planar (angle sum, 356°); the combination of diversely co-ordinated copper atoms, coupled with a quasi-boat conformation of the six-membered ring is presumably responsible for the very divergent Cu–Br–Cu angles noted above.

Complex (**2**).—The structure of this compound is quite unique. Both $[Co(S_2CNBu^n{}_2)_3]$ units have two of the three interligand 'chelate' sites involved in 'chelation' of copper atoms; as is usual, the 'chelating' sulphur atoms have long associated Co–S distances [2.263(3)—2.296(3), av. 2.28$_5$ Å] compared with the unchelated values [2.247(3)—2.267(3), av. 2.25$_5$ Å]; no structure determination is available for $[Co(S_2CNBu^n{}_2)_3]$, but ⟨Co–S⟩ in the Et_2 derivative (a similar straight chain alkyl substituted derivative which might be expected to be closely comparable) is 2.25$_8$ Å.[6] On each of the two $[Co(S_2CNBu^n{}_2)_3]$ units, we find one of the two chelation sites involved with a CuI_2Cu dimer [made up of Cu(4,5)I(4,5)], so that the basic constructional unit of the system may be considered to be a dimer of the type $[Co(S_2CNR_2)_3][CuI_2Cu][Co(S_2CNR_2)_3]$ previously observed as an isolated

Table 3. Metal atom environments in complex (**1**). The first column in each matrix is the metal–ligand distance (Å); other entries are angles (°) subtended at the metal by the relevant atoms at the head of each row and column

(*a*) Co

	$r_{\text{Co–S}}$	S(A2)	S(B1)	S(B2)	S(C1)	S(C2)
S(A1)	2.26(1)	77.3(4)	96.5(5)	92.6(5)	96.3(5)	169.6(3)
S(A2)	2.27(1)		170.2(5)	95.8(5)	92.5(4)	95.9(4)
S(B1)	2.28(1)			76.8(4)	95.6(5)	91.3(5)
S(B2)	2.30(1)				169.0(6)	95.9(5)
S(C1)	2.27(1)					76.0(4)
S(C2)	2.28(1)					

(*b*) Cu(1)

	$r_{\text{Cu–L}}$	S(B2)	Br(1)	Br(2)
S(A1)	2.40(1)	86.4(4)	105.3(2)	117.9(3)
S(B2)	2.41(1)		116.6(3)	109.1(4)
Br(1)	2.412(7)			117.8(3)
Br(2)	2.387(10)			

(*c*) Cu(2)

	$r_{\text{Cu–L}}$	Br(2)	N
Br(3)	2.346(6)	124.7(2)	124.9(9)
Br(2)	2.402(6)		108.5(9)
N	2.06(3)		

(*d*) Cu(3)

	$r_{\text{Cu–L}}$	S(C2$^{\text{I}}$)	Br(3)	Br(1)
S(B1$^{\text{I}}$)	2.39(1)	85.6(4)	111.4(4)	115.7(1)
S(C2$^{\text{I}}$)	2.41(1)		115.6(3)	105.5(3)
Br(3)	2.414(8)			118.4(3)
Br(1)	2.403(6)			

Cu(1)–Br(1)–Cu(3$^{\text{I}}$) 106.4(2); Cu(1)–Br(2)–Cu(2$^{\text{I}}$) 99.6(6); Cu(2)–Br(3)–Cu(3) 76.6(2)

Angles Co–S–C subtended at the sulphur atoms for S(A1, 2; B1, 2; C1, 2): 81(1), 84(1), 86(1), 87(1), 87(1), 88(1)

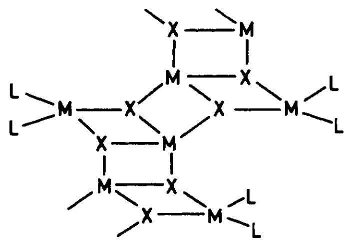
Cu(1)–S(A1)–Co 91.2(4), Cu(3$^{\text{I}}$)–S(B1)–Co 91.9(5)
Cu(1)–S(B2)–Co 89.8(5), Cu(3$^{\text{I}}$)–S(C2)–Co 91.1(4)
Cu(1)–S(A1)–C(A1) 98(1), Cu(3$^{\text{I}}$)–S(B1)–C(B1) 98(1)
Cu(1)–S(B2)–C(B1) 91(2), Cu(3$^{\text{I}}$)–S(C2)–C(C1) 98(1)

Transformation of the asymmetric unit: I $\bar{x}, \frac{1}{2} + y, \frac{1}{2} - z$.

Table 4. Cobalt environments in complex (**2**). $r_{\text{Co–S}}$ is the cobalt-sulphur distance (Å). Other entries are the angles (°) subtended at the cobalt atom by the relevant atoms at the head of the row and column. The two values in each entry are for molecules l = 1,2

	$r_{\text{Co–S}}$	S(lA2)	S(lB1)	S(lB2)	S(lC1)	S(lC2)
S(lA1)	2.287(3), 2.278(2)	75.94(9), 76.37(9)	98.27(10), 97.25(9)	169.68(8), 167.55(12)	95.32(9), 97.67(10)	93.69(9), 91.54(10)
S(lA2)	2.292(3), 2.263(3)		92.81(9), 93.34(11)	95.22(10), 93.07(10)	170.32(10), 171.41(12)	99.99(10), 97.44(10)
S(lB1)	2.286(3), 2.284(3)			76.57(10), 76.51(10)	92.58(11), 93.57(11)	164.27(11), 167.46(9)
S(lB2)	2.247(3), 2.267(3)				93.85(10), 93.50(10)	93.09(10), 96.44(10)
S(lC1)	2.247(3), 2.257(3)					76.11(10), 76.33(10)
S(lC2)	2.296(3), 2.294(3)					

species with R = n-propyl;[3] the dimensions of the latter about the $S_2CuI_2CuS_2$ core are similar to those of the present compound (Table 4), although about Cu(5) the two Cu–S distances are uncharacteristically disparate [2.385(3) and 2.530(2) Å]. Completion of the total polymer is achieved in two dimensions by a novel, centrosymmetric 'displaced step' unit, Cu_6I_6. This first of all links the dimeric units in a continuous one-dimensional strand, by means of Cu(1) and Cu(3) chelation, but simultaneously a pair of these strands is cross-linked so that the result is a double-stranded species. We know of no precedent for the Cu_6I_6 unit; the Cu_4X_4 'step' unit is familiar in a variety of complexes of Group 11 base adducts, both unidentate and more complex, and its extension to the infinite 'stair' arrays found in many 1 : 1 nitrogen base adducts is well known. Both types of array are generated by the linear addition of appropriate sequences of CuX units to a CuX_2Cu dimer; much less common are arrays in which CuX units are added not linearly, but at right angles, as in the 1 : 1 adduct of copper chloride with methyl isocyanide,[7] the 'displaced stair' polymer, still one-dimensional.



The present array may be considered representative of the basic constructional unit of this type of polymer, and may also be compared with the extended step Cu_6I_6 and Cu_8I_8 motifs found in the 1 : 0.5 adduct of copper(I) iodide with benzonitrile,[8] which are linear.

Table 5. Geometry of the copper iodide system in complex (**2**); distances in Å, angles in °

(*a*) The dimer

Cu(4)–I(4)	2.581(2)	Cu(5)–I(5)	2.591(2)	Cu(4)–S(1B1)	2.427(3)	Cu(5)–S(2C2)	2.530(2)
Cu(4)–I(5)	2.586(2)	Cu(4)–S(1A2)	2.429(3)	Cu(5)–S(2A1)	2.385(3)	Cu(4) ··· Cu(5)	2.750(2)
Cu(5)–I(4)	2.609(2)						
Cu(4)–I(4)–Cu(5)	63.99(6)	S(1A2)–Cu(4)–S(1B1)	86.12(9)	I(5)–Cu(5)–S(2A1)	117.18(8)	Cu(4)–S(1B1)–Co(1)	90.6(1)
Cu(4)–I(5)–Cu(5)	64.18(6)	I(4)–Cu(4)–I(5)	110.16(6)	I(5)–Cu(5)–S(2C2)	119.58(8)	Cu(5)–S(2A1)–C(2A1)	102.7(4)
I(4)–Cu(4)–S(1A2)	113.49(8)	I(4)–Cu(5)–I(5)	109.13(7)	Cu(4)–S(1A2)–C(1A1)	97.7(3)	Cu(5)*–S(2A1)–Co(2)	94.2(1)
I(4)–Cu(4)–S(1B1)	109.73(8)	S(2A1)–Cu(5)–S(2C2)	83.55(10)	Cu(4)–S(1A2)–Co(1)	90.4(1)	Cu(5)*–S(2C2)–C(23)	95.3(3)
I(5)–Cu(4)–S(1A2)	116.60(9)	I(4)–Cu(5)–S(2A1)	113.77(9)	Cu(4)–S(1B1)–C(1B1)	97.0(3)	Cu(5)*–S(2C2)–Co(2)	90.0(1)
I(5)–Cu(4)–S(1B1)	118.90(9)	I(4)–Cu(5)–S(2C1)	111.80(8)				

(*b*) The oligomer; italicized atoms are generated by the inversion centre

Cu(2)–I(3)	2.680(2)	Cu(2)–I(2)	2.578(2)	Cu(1)–S(2A2)	2.453(3)	Cu(2) ··· *Cu(2)*	3.096(2)
Cu(2)–*I(3)*	2.630(2)	Cu(2)–I(1)	2.851(1)	Cu(1)–S(2B1)	2.433(3)	Cu(2) ··· Cu(3)	2.744(2)
Cu(3)–I(3)	2.566(1)	Cu(1)–I(1)	2.602(2)	Cu(3)–S(1A1)	2.443(3)	Cu(2) ··· Cu(1)	2.824(2)
Cu(3)–I(1)	2.570(2)	Cu(1)–I(2)	2.536(1)	Cu(3)–S(1C2)	2.402(3)		
I(3)–Cu(2)–I(3)	108.69(6)	I(3)–Cu(3)–S(1A1)	107.14(7)	S(2A2)–Cu(1)–S(2B1)	85.21(10)	Cu(1)–S(2B1)–Co(2)	90.7(1)
I(3)–Cu(2)–I(2)	117.86(6)	I(3)–Cu(3)–S(1C2)	111.90(7)	Cu(3)–S(1A1)–C(1A1)	97.5(3)	Cu(1)–I(1)–Cu(2)	62.61(5)
I(3)–Cu(2)–I(1)	100.33(6)	S(1A1)–Cu(3)–S(1C2)	87.25(9)	Cu(3)–S(1A1)–Co(1)	89.1(1)	Cu(1)–I(1)–Cu(3)	105.08(5)
I(3)–Cu(2)–I(2)	111.45(6)	I(1)–Cu(1)–I(2)	117.05(7)	Cu(3)–S(1C2)–C(1C1)	96.6(3)	Cu(2)–I(1)–Cu(3)	60.56(5)
I(3)–Cu(2)–I(1)	110.31(6)	I(1)–Cu(1)–S(2A2)	110.44(8)	Cu(3)–S(1C2)–Co(1)	89.9(1)	Cu(1)–I(2)–Cu(2)	67.51(5)
I(2)–Cu(2)–I(1)	107.54(6)	I(1)–Cu(1)–S(2B1)	112.81(7)	Cu(1)–S(2A2)–C(2A1)	96.3(4)	Cu(2)–I(3)–Cu(3)	63.04(5)
I(1)–Cu(3)–I(3)	124.30(6)	I(2)–Cu(1)–S(2A2)	116.18(7)	Cu(1)–S(2A2)–Co(2)	90.7(1)	Cu(2)–I(3)–*Cu(2)*	71.31(6)
I(1)–Cu(3)–S(1A1)	113.44(7)	I(2)–Cu(1)–S(2B1)	110.96(7)	Cu(1)–S(2B1)–C(2B1)	97.0(3)	Cu(3)–I(3)–*Cu(2)*	105.06(5)
I(1)–Cu(3)–S(1C2)	106.66(8)						

Co(1) ··· Cu(3,4) 3.320(2), 3.352(2); Co(2) ··· Cu(1,5) 3.357(2), 3.415(3). * Symmetry transformation: $x, y - 1, z$.

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