(Cl)Os(pz)Ru$(NH_3)_5]^{5+}$, 114595-33-4; *cis*-$[(NH_3)_4$(Cl)Os(pz)Ru$(NH_3)_5]^{4+}$, 114595-34-5; *cis*-$[(NH_3)_4$(Cl)Os(pz)Ru$(NH_3)_5]^{3+}$, 114595-35-6; $[(NH_3)_5$Ru(pz)Ru$(NH_3)_5]Cl_6$, 94750-87-5; $[(NH_3)_5$Ru(pz)Ru$(NH_3)_5]I_5$, 104626-97-3; $[(NH_3)_5$Ru(pz)Ru$(NH_3)_5]I_4$, 114595-28-7; $[Os(NH_3)_5(OSO_2CF_3)](CF_3SO_3)_2$, 83781-30-0; $[Os(NH_3)_5(pz)](CF_3SO_3)_3$, 83781-35-5; $[Os(NH_3)_5(Etpz)]^{4+}$, 114595-30-1; $[Ru(NH_3)_6]^{3+}$, 18943-33-4; *cis*-$[(NH_3)_4(N_2)Os(pz)](BPh_4)_2$, 85282-29-7; $[Rh(NH_3)_5(OSO_2CF_3)](CF_3SO_3)_2$, 84254-57-9; $[Ru(NH_3)_5(OSO_2CF_3)](CF_3SO_3)_2$, 84278-98-8; $[Rh(NH_3)_5(pz)]^{2+}$, 114595-32-3; D_2, 7782-39-0.

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A Novel Series of 1:1, 2:1, and 3:1 Heterobimetallic Adducts from the Reaction of Copper(I) Halides with Tris(dithiocarbamato)cobalt(III) Complexes[†]

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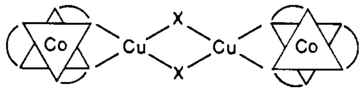
The tendency for neutral dithiocarbamate complexes, $M(S_2CNR_2)_n$, to act as chelating ligands via the sulfur atoms to form heterometallic adducts is relatively unexplored, and only a small number of such compounds have been well characterized.[1-3] We have obtained very small crystals of the 1:1 adducts of CuBr with $Co(S_2CN(CH_2)_4)_3$[2] and of CuI with $Co(S_2CN$-*n*-$Pr_2)_3$ and $Co(S_2CN$-*i*-$Pr_2)_3$[3] by slow interdiffusion of the appropriate copper and cobalt compounds. Structural studies on these compounds have shown that two $Co(S_2CNR_2)_3$ molecules chelate to a Cu_2X_2 dimer to form molecules of the type



in which the $Co(S_2CNR_2)_3$ molecules may be of similar or opposed chirality.

In these compounds, only one of the three possible interligand S···S chelating sites is employed. We have now isolated the compounds $[CuBr]_2[Co(S_2CNEt_2)_3]\cdot 2CH_3CN$ (**1**) and $[CuI]_3[Co(S_2CN(CH_2)_4)_3]$ (**2**), in which respectively two and three of the possible sites are utilized to give adducts of 2:1 and 3:1 stoichiometry. We have also found that for several cobalt(III) dithiocarbamate complexes, no adduct formation takes place at all.

Experimental Section

Synthesis. Small dark brown crystals of **1** are formed slowly after a period of days by allowing a dilute solution of $Co(S_2CNEt_2)_3$ in CH_3CN to stand over solid CuBr under an argon atmosphere. During this period the solution changes color from green to deep brown. The crystals are relatively stable to air, slowly losing solvent to give amorphous powders. Small dark brown/black crystalline needles of **2** could be prepared by the slow interdiffusion of dilute solutions of CuI in CH_3CN and $Co(S_2CN(CH_2)_4)_3$ in CH_2Cl_2 in a variety of stoichiometric ratios. Attempts to form an adduct of $Co(S_2CN(CH_4)_2)_3$ with CuCl, or adducts of $Co(S_2CNH_2)_3$, $Co(S_2CNMePh)_3$, $Co(S_2CNPh_2)_3$, $Co(S_2CNBz_2)_3$ or $Co(S_2COEt)_3$ with either CuBr or CuI were unsuccessful. In each case no reaction was observed to take place, either by color changes in the reaction mixture or by the precipitation of crystalline material other than the parent compounds. With $Co(S_2CNMe_2)_3$ and CuI very small, fragile crystals were obtained and these were isomorphous with **2**. [space group $I\bar{4}3d$, $a = 23.31$ (1) Å; a structure determination carried out on data to $2\theta_{max} = 40°$ (341 "observed" reflections, $R = 0.087$) establishing its essential similarity.]

Table I. Crystal Data for Compounds **1** and **2**

	1	**2**
stoichiometry	$[Co(dtc)_3]\cdot 2CuBr\cdot 2MeCN$	$[Co(dtc)_3]\cdot 3CuI$
ligand substituent	C_2H_5	$(CH_2)_4$
formula	$C_{19}H_{36}Br_2CoCu_2N_5S_6$	$C_{15}H_{24}CoCu_3I_3N_3S_6$
M_r	872.7	1069.1
cryst syst	monoclinic	cubic
space group	$C2/c$; No. 15	$I\bar{4}3d$; No. 220
a, Å	18.91 (2)	23.637 (10)
b, Å	14.583 (4)	
c, Å	13.705 (8)	
β, deg	118.82 (6)	
V, Å^3	3312 (2)	13 207 (10)
D_{calcd}, g cm^{-3}	1.75	2.15
D_{measd}, g cm^{-3}	...	2.16 (1)
Z	4	16
$F(000)$	1744	8064
μ_{Mo}, cm^{-1}	48	57
specimen dimens, mm	0.15 × 0.07 × 0.07	0.30 × 0.20 × 0.15
A^*: min, max	...	1.72, 1.91
$2\theta_{max}$, deg	45	60
N	2154	1716
N_o	1101	905
n_v	160	95
R	0.049	0.051
R_w	0.040	0.054

Structure Analysis. Unique data sets were measured at 295 K to the specified $2\theta_{max}$ limits by using Syntex $P2_1$ and ENRAF-Nonius CAD-4 four-circle diffractometers (monochromatic Mo Kα radiation sources, $\lambda = 0.7106_9$ Å) operating in conventional $2\theta/\theta$ scan mode. N independent reflections were obtained, N_o with $I > 3\sigma(I)$ being considered "observed" and used in the full-matrix least-squares refinement, minimizing $\sum w\Delta F^2$. Difference map artifacts in **1** were successfully modeled as acetonitrile solvent with assignment of C and N derived from the behavior of geometric, thermal, and statistical parameters. Remaining difference map residues were assigned as hydrogen atoms in the latter stages of refinement. Data for **2** were corrected for absorption (analytical correction). Anisotropic thermal parameters were refined for the non-hydrogen atoms (in the preferred enantiomeric setting for **2**). x, y, z, and U_{iso} for hydrogen were constrained to estimated values. Residuals on $|F|$ at convergence were R and R_w; statistical weights used were derived from $\sigma^2(I) = \sigma^2(I_{diff}) + 0.0001\sigma^4(I_{diff})$. Each structure refined smoothly in the chosen space group with no anomalies with respect to features such as thermal envelopes or disorder. Neutral-atom complex scattering factors were employed;[4] computation used the XTAL programme system[5] implemented by S. R. Hall on a Perkin-Elmer 3241 computer. Crystal and refinement data are given in Table I. Non-hydrogen atom coordinates for **1** and **2** are listed in Tables II and III and relevant geometric parameters are given in Table IV.

[†] Lewis-Base Adducts of Group 11 Metal(I) Compounds. 39.

[‡] University of Western Australia.

[§] Griffith University.

(1) (a) Cras, J. A.; Willemse, J. *J. Inorg. Nucl. Chem.* **1977**, *39*, 1226. (b) McCleverty, J. A.; McLuckie, S.; Morrison, N. J.; Bailey, N. A.; Walker, N. W. *J. Chem. Soc., Dalton Trans.* **1977**, 359.

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Table II. Non-Hydrogen Atom Coordinates for **1**

atom	*x*	*y*	*z*
Br	−0.30746 (8)	0.8370 (1)	0.0461 (1)
Cu	−0.1741 (1)	0.7933 (1)	0.0728 (2)
Co	0	0.8971 (2)	$^1/_4$
		Ligand 1	
S(11)	−0.0663 (2)	0.7742 (3)	−0.2705 (3)
C(11)	0	0.7074 (15)	$^1/_4$
N(1)	0	0.6162 (13)	$^1/_4$
C(12)	0.0636 (10)	0.5636 (12)	0.2396 (18)
C(13)	0.0355 (12)	0.5274 (18)	0.1347 (21)
		Ligand 2	
S(21)	−0.0952 (2)	0.9178 (2)	0.0674 (3)
S(22)	−0.0824 (2)	1.0032 (3)	0.2598 (3)
C(21)	−0.1356 (7)	1.0015 (9)	0.1156 (11)
N(2)	−0.1941 (6)	1.0568 (8)	0.0547 (10)
C(22)	−0.2193 (9)	1.1277 (11)	0.1075 (13)
C(23)	−0.2786 (9)	1.0956 (13)	0.1431 (14)
C(24)	−0.2335 (9)	1.0504 (11)	−0.0665 (13)
C(25)	−0.2025 (11)	1.1177 (13)	−0.1160 (13)
		Acetonitrile	
N	0.590 (1)	0.807 (2)	0.384 (2)
C(1)	0.539 (1)	0.776 (2)	0.393 (2)
C(2)	0.473 (1)	0.739 (1)	0.404 (2)

Table III. Non-Hydrogen Atom Coordinates for **2**

atom	*x*	*y*	*z*
I	−0.00685 (6)	0.08561 (5)	−0.21847 (5)
Cu	−0.02524 (11)	−0.01923 (9)	−0.19551 (9)
Co	−0.07747 (9)	*a*	*a*
S(1)	−0.1177 (2)	−0.0439 (2)	−0.1575 (2)
S(2)	−0.1059 (2)	0.0125 (2)	−0.0531 (2)
C	−0.1296 (7)	0.0173 (6)	−0.1222 (7)
N	−0.1531 (6)	0.0605 (6)	−0.1436 (5)
C(1)	−0.1583 (10)	0.1189 (10)	−0.1184 (10)
C(2)	−0.1684 (11)	0.1591 (10)	−0.1627 (8)
C(3)	−0.1958 (12)	0.1251 (11)	−0.2078 (12)
C(4)	−0.1751 (8)	0.0627 (9)	−0.2021 (8)

[a] Symmetry related: $x = y = z$.

X-ray Photoelectron Spectroscopy. XPS measurements on **2**, the "parent" compounds CuI and $Co(S_2CN(CH_2)_4)_3$, and copper metal were recorded on a PHI 560 system with a base vacuum of 10^{-9} Torr although most runs were carried out at somewhat lower vacuum due to sample outgassing. Fresh and clean surfaces were prepared by grinding the samples in a mortar and pestle and attaching the resultant powder to 3M copper-backed adhesive tape. The Al Kα line (1486.6 eV) at a source power of 300 W was used. Survey scans were obtained over the binding energy range 0–1000 eV in steps of 0.5 eV with a constant analyzer energy of 100 eV. Detailed scans were also carried out over the relevant peaks in steps of 0.2 eV and a CAE of 25 eV. Signal to noise ratios were improved by repetitive scanning. For all samples, except Cu and CuI, static charging shifts of 2–3 eV were observed in the peak positions. Corrections were made by assigning a binding energy of 284.8 eV to the carbon 1s peak.[6] Higher binding energy shoulders were observed in the C(1s) peak due, presumably, to adsorbed surface contaminants such as CO_2. The data were smoothed with a seventh-order polynomial fitting routine but were not processed in any other fashion. Binding energy data are tabulated in Table V.

Results and Discussion

Structural Results. The asymmetric unit of **1** consists of one CuBr unit, one CH_3CN molecule, and half of a $Co(S_2CNEt_2)_3$ molecule, the latter being disposed on a crystallographic 2 axis. The CuBr unit lies about an inversion center forming a planar Cu_2Br_2 dimer with two associated $Co(S_2CNEt_2)_3$ molecules of opposite chirality (Figure 1). For comparison, the Cu_2Br_2 dimer in $\{[CuBr][Co(S_2CN(CH_2)_4)_3]\}_2$ (**3**) contains no crystallographically imposed symmetry and is quite bent.[2] There are observable differences in the geometries of the two dimers (Table IV). The range of Cu–Br distances is considerably smaller in **3**, and the Cu⋯Cu distance increases from 2.697 (2) Å in **3** to 2.880 (3) Å in **1**. Larger variations in core geometries have also been observed in the 1:2 binuclear adducts of 2-methyl- and 2,4-dimethyl-substituted pyridine bases with CuBr. It is likely that these structural changes are dependent on the size and steric profile of the peripheral ligands.[7] In the present case the change in steric profile occurs in changing the substituent group from tetramethylene to diethyl.

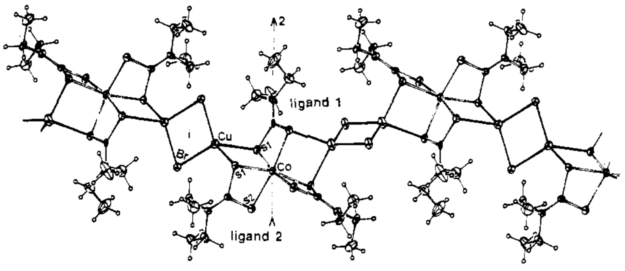

Figure 1. Polymer of **1** with the *a* axis horizontal. 20% thermal ellipsoids are shown for the non-hydrogen atoms, together with the labeling of the asymmetric unit. Hydrogen atoms have arbitrary radii of 0.1 Å.

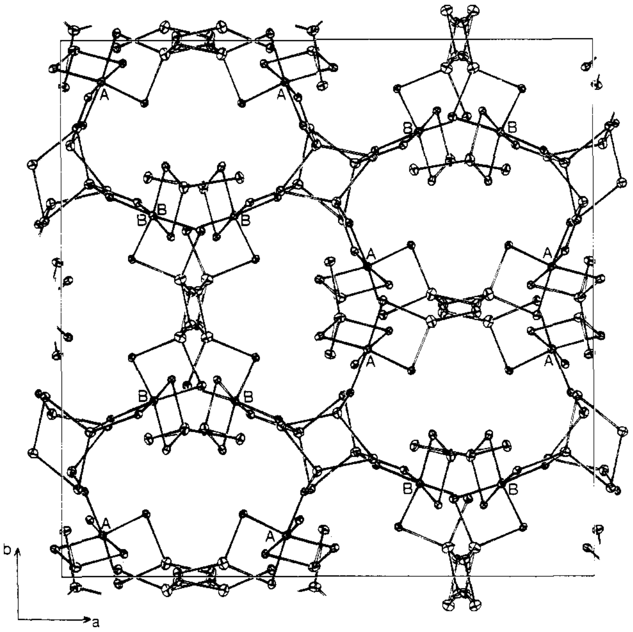

Figure 2. Unit cell contents of **2** projected down the cubic axis. The two sets of cobalt atoms of opposed chirality are denoted A and B. Only I, Cu, Co, and S atoms are shown, with thermal ellipsoids at the 20% probability level.

In **1**, there is a difference of ca. 0.04 Å between the Co–S distances for the sulfur atoms chelated to the copper (2.281 (5) and 2.292 (4) Å) and the unchelated sulfurs (2.245 (5) Å) whereas in the parent complex the Co–S distances are covered by the narrow range 2.265 (1)–2.268 (1) Å.[8] The overall ligand geometries in both complexes are, however, very similar. The CH_3CN molecule occupies voids in the lattice in the region where the sulfur atoms are not coordinated to the cuprous halide.

The asymmetric unit of **2** comprises one-third of the $Co(S_2CN(CH_2)_4)_3$ molecule, with the cobalt atom located on a crystallographic threefold axis and half of a Cu_2I_2 dimeric unit disposed about a crystallographic twofold axis. The Cu⋯Cu′ "axis" is disposed close to each twofold axis of the idealized D_3 point symmetry of the associated symmetry-related dithiocarbamate molecules. The nature of the polymer formed by the bridging of the cobalt dithiocarbamate molecules by the CuI_2Cu dimers

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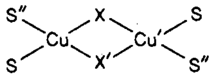
Table IV. Geometric Parameters for $Cu_2X_2S_4$ (X = Br, I)



	Br			I		
	1	3^a		2	4^b	5^b
Cu–X	2.451 (4)	2.456 (1)	2.463 (1)	2.574 (5)	2.575 (2)	2.594 (3)
Cu–X′	2.417 (3)	2.482 (1)	2.421 (1)	2.605 (5)	2.583 (1)	
Cu–S	2.374 (5)	2.431 (2)	2.390 (2)	2.434 (5)	2.420 (4)	2.435 (7)
Cu–S″	2.500 (4)	2.393 (2)	2.399 (2)	2.474 (5)	2.417 (3)	
Cu···Cu′	2.880 (3)	2.697 (2)		2.732 (3)	2.752 (2)	2.765 (5)
X···X′	3.925 (3)	4.013 (1)		4.313 (2)	4.363 (1)	4.391 (4)
Co···Cu	3.365 (3)	3.330 (1)	3.286 (1)	3.348 (1)	3.330 (9)	3.301 (5)
Cu–X–Cu′	72.53 (9)	66.50 (4)	66.73 (4)	63.67 (8)	64.5 (2)	64.4 (1)
S–Cu–S″	85.6 (1)	86.50 (6)	88.98 (7)	85.9 (2)	87.2 (4)	87.7 (2)

[a] Reference 2. [b] Reference 3.

Table V. X-ray Photoelectron Spectroscopic Binding Energies

	binding energies, eV				
compd	$Cu(2p_{3/2})$	$I(3d_{5/2})$	$Co(2p_{3/2})$	S(2p)	N(1s)
Cu	932.8				
CuI	932.0	619.4			
$Co(S_2CN(CH_2)_4)_3$			779.4	161.9	399.3
2	932.1	618.6	779.3	162.5	399.7

is both complex and interesting. In space group $I\bar{4}3d$ there are 16 Wyckoff *c* sites of 3 symmetry associated with the cobalt atoms, comprising two sets of opposite chirality, denoted A and B in Figure 2. The network of this figure may be dissected into two totally independent three-dimensional meshes associated with each of the two types of cobalt dithiocarbamate. Within either one of the two polymers all cobalt environments are of the same chirality. The CuI_2Cu dimer in **2** is appreciably bent with a dihedral angle of 35.9° at the I_2 line contrasting with the planar moieties found in $\{[CuI][Co(S_2CN\text{-}n\text{-}Pr_2)_3]\}_2$ (**4**) and $\{[CuI][Co(S_2CN\text{-}i\text{-}Pr_2)_3]\}_2$ (**5**).[3] However, there is very little difference overall in the dimer geometries of the three complexes (Table IV).

In this compound, although all six sulfur atoms are coordinated to copper, the two independent Co–S distances of 2.259 (1) and 2.304 (5) Å are markedly different and comparable to the range of 2.258 (2)–2.307 (2) Å found in **3** where only one S···S site is chelated to the copper halide dimer. These results indicate that coordination to the copper halide alone is not the primary condition leading to variations in the Co–S distances found for these compounds and that overall packing requirements of the lattice are likely to be just as important.

X-ray Photoelectron Spectroscopy. In the X-ray photoelectron spectrum of **2**, the binding energies of the Cu(2p) manifold were not significantly different from those observed for CuI with binding energy values of 932.1 and 932.0 eV for the $Cu(2p_{3/2})$ bands. Similarly, the Co(2p) bands were found to be virtually identical for **2** and $Co(S_2CN(CH_2)_4)_3$ (Table V). In the S(2p) band, the binding energies increased from 161.9 to 162.5 eV on adduct formation. For comparison, differences in the binding energies between ionic dithiocarbamate salts and the corresponding cobalt complexes are ca. 1.0 eV with a value of 161.0 eV being recorded for $Na[S_2CN(CH_2)_4]$ and 160.9 eV for $[Co(diNOsar)][S_2CN(CH_2)_4]_3$.[9] For $[Co_2(S_2CNEt_2)_5][BF_4]$ in which the dithiocarbamate ligands also bridge between two metal atoms,[10] the S(2p) binding energy was found to be 162.2 eV. These shifts are small but consistently to higher binding energies as the number of atoms coordinated to the sulfur atoms increases. Similarly, the $I(3d_{5/2})$ peak shifts from 619.4 eV for CuI where the iodide atom is coordinated to four copper atoms to 618.6 eV in **2** where the iodide is coordinated to only two copper atoms.

Increased binding energies usually reflect decreased electron density on the atom concerned, and the effects observed here are consistent with a transfer of electron density away from the sulfur or iodide atoms as the coordination number increases.

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Registry No. **1**, 114132-45-5; **2**, 114132-46-6; $Co(S_2CNEt_2)_3$, 13963-60-5; $Co(S_2CN(CH_2)_4)_3$, 24412-38-2; CuI, 7681-65-4.

Supplementary Material Available: Tables SUP-I–SUP-VI, listing thermal and hydrogen parameters and ligand geometries (6 pages); tables of calculated and observed structure factor amplitudes (14 pages). Ordering information is given on any current masthead page.

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Synthesis, Electrochemistry, and Spectroelectrochemistry of (P)Ge(Fc)$_2$ and (P)Ge(C_6H_5)(Fc): First Example of Metal-Carbon-σ-Bonded Porphyrins with Two Different Axial Groups

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In a preliminary communication the oxidative electrochemistry of $(OEP)Ge(Fc)_2$ in methylene chloride was reported where OEP is the dianion of octaethylporphyrin and Fc is a σ-bonded ferrocenyl group.[2] The half-wave potential for the first oxidation of this complex is negatively shifted by up to 350 mV with respect to $E_{1/2}$ for oxidation of free ferrocene under the same solution conditions. The electrooxidized $[(OEP)Ge(Fc)_2]^+$ and $[(OEP)Ge(Fc)_2]^{2+}$ cations were stable due to a delocalization of positive charge that occurs from the axial ferrocenyl group onto the porphyrin macrocycle. It was not clear if this stability would also be observed for $(P)Ge(Fc)_2$ complexes with other less basic porphyrin macrocycles or for σ-bonded Fc complexes of the type (P)Ge(R)(Fc) where R is an aryl or alkyl group. This is investigated in the present paper, which describes the detailed electrochemistry and spectroelectrochemistry of $(P)Ge(Fc)_2$ and $(P)Ge(C_6H_5)(Fc)$, where P is the dianion of octaethylporphyrin (OEP) or tetraphenylporphyrin (TPP). The $(P)Ge(C_6H_5)(Fc)$ complexes represent the first examples of metalloporphyrins

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[2] Kadish, K. M.; Xu, Q. Y.; Barbe, J.-M. *Inorg. Chem.* **1987**, *26*, 2565.