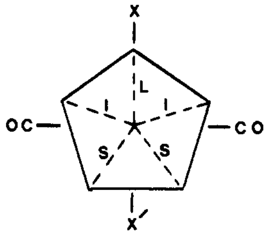
the C=O bond in organic carbonates (ca. 1.16 Å).[18] The remaining two C—O bond lengths (average 1.30 Å) are slightly shorter than the C—O bonds in organic carbonates (1.28-1.37 Å, average 1.34 Å). The angles about the carbonato carbon (C16) are comparable to those in ethylene and vinylene carbonate.[18]

The distances from Mo to the Cp carbons and the C-C distances within the Cp ring show some interesting variations (Figure 3). Such alterations in bond lengths have been treated theoretically,[16,19,20] but the simplest rationalization of the observed trends in the Mo-C distances is that the longer Mo-C distances "trans" (Figure 3) to the carbonyls are a manifestation of the trans influence commonly seen in square-planar complexes (see discussion in ref 21). In all the structures of the type *cis*-CpM(CO)$_2$L$_2$, the M-C(Cp) bond length pattern is as in Figure 3. In *trans*-CpM(CO)$_2$XX′, the pattern appears to be that shown in **8**, where X′ is higher in the spectrochemical series than X (L = long, I = intermediate, S = short). The same pattern is seen in CpMo(CO)$_3$X complexes (let X′ = CO in **8**).[22,23]

**Reactivity.** Only a few reactions of the carbonato anion, **1**, have been investigated. Treatment of **1** with trifluoroacetic acid in the presence of Ph$_3$P, Et$_3$P, or (MeO)$_3$P gave corresponding *cis*-CpMo(CO)$_2$L$_2^+$ complexes, identified by IR spectra.[24] Presumably, the carbonato group is protonated and then lost as CO$_2$ and water:



8

$$CpMo(CO)_2(\eta^2\text{-}O_2CO)^- + 2H^+ + 2L \rightarrow H_2O + CO_2 + CpMo(CO)_2L_2^+ \quad (2)$$

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**Supplementary Material Available:** Tables VI and VII, giving H atom positions and $F_o$ vs. $F_c$ values (13 pages). Ordering information is given on any current masthead page.

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# Lewis Base Adducts of Group 11 Metal Compounds.[†] 10. The 1:1 Heterobimetallic Adduct of Tris(pyrrolidinecarbodithioato)cobalt(III) with Copper(I) Bromide

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Reaction of copper(I) bromide with tris(pyrrolidinecarbodithioato)cobalt(III) has yielded a 1:1 adduct that has been characterized by single-crystal X-ray structure determination. Crystals are triclinic, $P\bar{1}$, $a$ = 15.385 (4) Å, $b$ = 15.025 (4) Å, $c$ = 11.088 (4) Å, $\alpha$ = 76.01 (2)°, $\beta$ = 79.67 (2)°, and $\gamma$ = 78.18 (2)°; the structure was refined by least-squares methods to a residual of 0.036 for 4369 independent observed reflections. The complex is dimeric, of the type (Co(dtc)$_3$)CuBr$_2$Cu(Co(dtc)$_3$), with two such units in the cell. The copper is four-coordinate by two bromine atoms and two sulfur atoms from independent carbodithioate ligands, the approach of the copper to the latter being along the pseudo-2-fold axis of the Co(dtc)$_3$ species. Cu···Cu is 2.697 (2) Å.

## Introduction

In the more symmetrical pseudo-square-planar and pseudo-$D_3$ ("octahedral") bis- and tris(1,1-dithio chelate)metal complexes, each of the sulfur atoms is coordinated to only one metal atom; it is well-known that the bonding capacities of these sulfur atoms is not saturated since it is possible for them to be utilized for bridging purposes to yield oligonuclear species as in, e.g., [Ru$_2$(S$_2$CN-*i*-Pr$_2$)$_5$]$^+$, [Ru$_2$(CO)$_2$(S$_2$CNEt$_2$)$_4$], and [Ru$_3$(CO)$_3$Cl$_2$(S$_2$C·NEt$_2$)$_4$].[2] Apart from a number of well-studied examples of oligomer formation of this type in homonuclear systems, however, little advantage appears to have been taken of the apparent capacity of such species to enable the coordination complex itself to act as a chelating agent for the purpose of coordinating other metals to form heteronuclear species. Within the 1:1 dithio chelate field, the only example structurally characterized that appears to exploit this possibility is that of [Fe[CN(*p*-ClC$_6$H$_4$)]$_2$(S$_2$CNEt$_2$)$_2$ZnI$_2$],[3] wherein the zinc atom becomes four-coordinate by chelation by a pair of sulfur atoms from different carbodithioate ligands. More conventional bridging thiol groups are to be found in species such as [[(piperidine *N*-oxide-(1−))$_2$Mo($\mu$-S)$_2$Cu $\mu$-Cl]$_2$].[4] We find that the addition of tris(N,N- disubstituted carbodithioato)cobalt(III) complexes dissolved in acetonitrile to solutions of copper(I) halide in the same solvent yield dark amorphous precipitates. Crystalline compounds may be obtained by taking the solvent in a flat dish and allowing the two species to slowly diffuse together from deposits of solid at the extremities of the dish, air being excluded. In this manner an adduct of tris(pyrrolidinecarbodithioato)cobalt(III)(Co(dtc)$_3$) with

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[†] The group notation is being changed in accord with recent actions by IUPAC and ACS nomenclature committees. A and B notation is being eliminated because of wide confusion. Group I becomes groups 1 and 11, group II becomes groups 2 and 12, group III becomes groups 3 and 13, etc.

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Table I. Non-Hydrogen Atom Coordinates

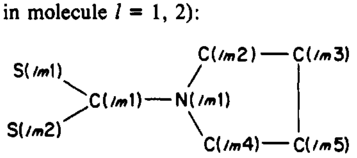
| | molecule $l = 1$ | | | molecule $l = 2$ | | |
|---|---|---|---|---|---|---|
| atom | $x$ | $y$ | $z$ | $x$ | $y$ | $z$ |
| Cu($l$) | 0.94058 (6) | 0.81363 (5) | 0.23080 (7) | 0.79566 (6) | 0.76989 (5) | 0.16773 (8) |
| Br($l$) | 0.78869 (5) | 0.09211 (4) | 0.26604 (6) | 0.94599 (5) | 0.72551 (4) | 0.06614 (6) |
| Co($l$) | 1.12229 (6) | 0.79007 (5) | 0.36736 (6) | 0.62017 (6) | 0.67135 (5) | 0.18752 (6) |
| Ligand $m = 1$ | | | | | | |
| S($l$11) | 1.06814 (11) | 0.89300 (9) | 0.19985 (11) | 0.72967 (12) | 0.64876 (10) | 0.31390 (12) |
| S($l$12) | 1.18745 (12) | 0.72206 (10) | 0.20289 (13) | 0.72110 (13) | 0.55041 (10) | 0.12966 (14) |
| C($l$11) | 1.1321 (4) | 0.8162 (3) | 0.1112 (4) | 0.7851 (5) | 0.5612 (4) | 0.2348 (5) |
| N($l$11) | 1.1346 (3) | 0.8309 (3) | −0.0112 (4) | 0.8642 (4) | 0.5138 (3) | 0.2530 (4) |
| C($l$12) | 1.0800 (4) | 0.9117 (4) | −0.0836 (5) | 0.9188 (5) | 0.5252 (4) | 0.3404 (6) |
| C($l$13) | 1.0898 (6) | 0.8868 (5) | −0.2095 (5) | 1.0128 (6) | 0.4853 (5) | 0.2895 (7) |
| C($l$14) | 1.1697 (6) | 0.8190 (6) | −0.2190 (6) | 0.9997 (6) | 0.4105 (5) | 0.2287 (7) |
| C($l$15) | 1.1836 (4) | 0.7649 (4) | −0.0885 (5) | 0.9130 (5) | 0.4480 (4) | 0.1745 (5) |
| Ligand $m = 2$ | | | | | | |
| S($l$21) | 1.23980 (12) | 0.85918 (10) | 0.37095 (13) | 0.53029 (13) | 0.58614 (10) | 0.33436 (13) |
| S($l$22) | 1.20177 (12) | 0.68396 (9) | 0.50858 (13) | 0.51688 (12) | 0.65124 (10) | 0.07624 (13) |
| C($l$21) | 1.2716 (5) | 0.7622 (4) | 0.4837 (5) | 0.4723 (5) | 0.5876 (4) | 0.2155 (5) |
| N($l$21) | 1.3397 (4) | 0.7528 (3) | 0.5450 (5) | 0.4047 (4) | 0.5440 (3) | 0.2296 (4) |
| C($l$22) | 1.3954 (5) | 0.8224 (5) | 0.5323 (6) | 0.3636 (5) | 0.4967 (4) | 0.3528 (5) |
| C($l$23) | 1.4727 (6) | 0.7704 (7) | 0.6035 (8) | 0.2805 (6) | 0.4717 (6) | 0.3251 (7) |
| C($l$24) | 1.4306 (6) | 0.6983 (6) | 0.7058 (7) | 0.2986 (6) | 0.4671 (6) | 0.1904 (7) |
| C($l$25) | 1.3666 (5) | 0.6689 (5) | 0.6396 (6) | 0.3599 (5) | 0.5371 (4) | 0.1267 (5) |
| Ligand $m = 3$ | | | | | | |
| S($l$31) | 1.03207 (12) | 0.86900 (9) | 0.50480 (13) | 0.54492 (13) | 0.80657 (10) | 0.23883 (14) |
| S($l$32) | 0.99728 (11) | 0.71994 (9) | 0.41664 (12) | 0.68277 (12) | 0.78445 (10) | 0.03715 (13) |
| C($l$31) | 0.9557 (5) | 0.8014 (3) | 0.5108 (5) | 0.6102 (4) | 0.8628 (4) | 0.1155 (5) |
| N($l$31) | 0.8753 (4) | 0.8079 (3) | 0.5749 (4) | 0.6083 (4) | 0.9534 (3) | 0.0848 (4) |
| C($l$32) | 0.8382 (6) | 0.8839 (5) | 0.6440 (7) | 0.5521 (5) | 1.0176 (4) | 0.1599 (7) |
| C($l$33) | 0.7419 (8) | 0.8788 (6) | 0.6687 (10) | 0.5785 (9) | 1.1083 (5) | 0.0973 (9) |
| C($l$34) | 0.7266 (7) | 0.7915 (8) | 0.6542 (12) | 0.6493 (7) | 1.0989 (5) | 0.0012 (11) |
| C($l$35) | 0.8095 (5) | 0.7494 (4) | 0.5810 (6) | 0.6691 (5) | 1.0007 (4) | −0.0169 (6) |

copper(I) bromide has been obtained as a black finely crystalline air-stable solid, as we demonstrate by the single-crystal X-ray structure determination that we report in this paper.

## Crystallography

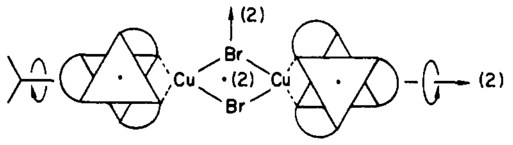
**Crystal Data**: $C_{15}H_{24}BrCoCuN_3S_6$, mol wt 641.2, triclinic, space group $P\bar{1}$ ($C_i^1$, No. 2), $a = 15.385$ (4) Å, $b = 15.025$ (4) Å, $c = 11.088$ (4) Å, $\alpha = 76.01$ (2)°, $\beta = 79.67$ (2)°, $\gamma = 78.18$ (2)°, $V = 2412$ (1) Å$^3$, $Z = 4$, $D_{\text{calcd}} = 1.77$ g cm$^{-3}$, $F(000) = 1288$; specimen irregular fragment, ca. 0.2 mm diameter, $\mu_{\text{Mo}} = 39$ cm$^{-1}$, $2\theta_{\text{max}} = 50°$; $N$, $N_o$ = 5938, 4369; $R$, $R'$ = 0.036, 0.044.

**Structure Determination.** A unique data set was measured at 295 K within a preset $2\theta_{\text{max}}$ limit on a Syntex P2$_1$ four-circle diffractometer fitted with a monochromatic Mo K$\alpha$ radiation source ($\lambda = 0.71069$ Å) and 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 (basically) 9 × 9 block-diagonal least-squares refinement without absorption correction following solution of the structure by vector methods. Anisotropic thermal parameters were refined for the non-hydrogen atoms; $(x, y, z, U_{\text{iso}})_H$ were constrained at estimated values. Residuals on $F$ quoted at convergence are conventional $R$, $R'$, reflection weights $(\sigma^2(F_o + 0.0005(F_o)^2)^{-1}$. Neutral complex scattering factors were used;[5] computation used the X-RAY 76 program system[6] implemented on a Perkin-Elmer 3240 computer by S. R. Hall. Non-hydrogen atom labeling in the carbodithioate ligands and the molecules is as follows (for ligand $m$ = 1–3 in molecule $l$ = 1, 2):



## Discussion

The structure determination establishes the presence of tris(pyrrolidinecarbodithioato)cobalt(III) and copper(I) bromide in a 1:1 stoichiometry (Figure 1; Table I). The overall molecular aggregate, however, is a dimeric $(Co(dtc)_3{\cdot}CuBr)_2$ unit that also comprises the asymmetric unit of the structure. It consists of a central dibromo-bridged $CuBr_2Cu$ core, with the remaining two coordination sites of each four-coordinate copper atom occupied by a sulfur atom from each of the upper and lower triangular faces of the tris(chelate)cobalt(III) system:



The chirality of the two $Co(dtc)_3$ systems is the same, so that the overall aggregate is also chiral, with potential 222 symmetry as shown, the 2 axes being coincident with those of the central $CuBr_2Cu$ core and also with one of the potential 2 axes of the $Co(dtc)_3$. The crystal as a whole, of course, is a racemate, belonging to a centrosymmetric space group. In the above diagram, the potential 3-fold axes of the $Co(dtc)_3$ molecules considered in isolation lie parallel to one of the potential 2 axes of the aggregate; in reality this parallelism is lost by rotation of the $Co(dtc)_3$ molecules in mutually opposite directions about the overall 2 axis passing through the cobalt atoms, so that the two $CuS_2$ coordination planes can become parallel to each other and normal to the $CuBr_2Cu$ plane. In this process, equal and opposite rotations of the two $Co(dtc)_3$ molecules preserve the overall 222 symmetry of the aggregate. This idealized symmetry is lost in a number of ways, however.

(a) The central $CuBr_2Cu$ system is not planar, $\sigma$ for the array being 0.24$_9$ Å with atom deviations of ±0.21–0.22 Å. The two $CuBr_2$ planes meet with a dihedral angle of 35.4° at the Br···Br line. A high degree of equivalence is preserved, however, between the notionally equivalent distances and angles of the $CuBr_2Cu$ core (Table II). The deviation of the associated cobalt atom from each $CuBr_2$ plane is minor (0.110 and 0.079 Å, respectively).

(b) The (acute, moduli) torsion angles defined by the BrCuCoX systems of each molecular half (X being the centroid of the $S_3$ face of the coordination sphere of the cobalt corresponding to the

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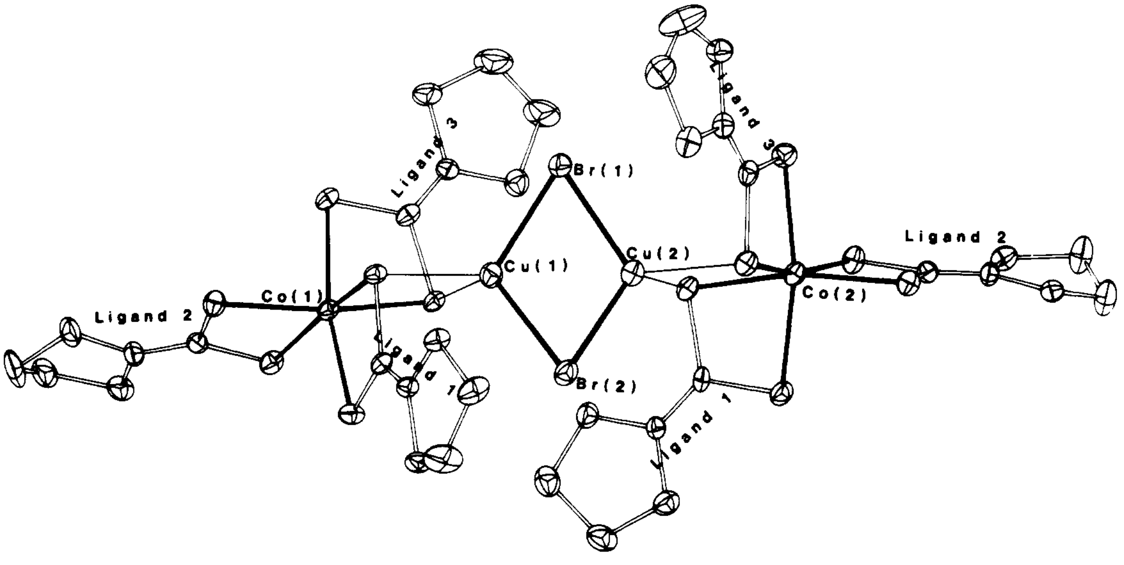

**Figure 1.** Projection of the dimer normal to the Cu$_2$Br$_2$ plane. 20% thermal ellipsoids are shown for the non-hydrogen atoms together with atom numbering.

Table II. Heavy-Atom Geometry

| | *l* = 1 | *l* = 2 | | *l* = 1 | *l* = 2 |
|---|---|---|---|---|---|
| | | Distances (Å) | | | |
| Cu···Cu | 2.697 (2) | | Co(*l*)–S(*l*11) | 2.275 (2) | 2.302 (2) |
| Br···Br | 4.013 (1) | | Co(*l*)–S(*l*12) | 2.281 (2) | 2.275 (2) |
| Cu(*l*)–Br(*l*) | 2.456 (1) | 2.421 (1) | Co(*l*)–S(*l*21) | 2.272 (2) | 2.261 (2) |
| Cu(*l*)–Br(*l*′) | 2.482 (1) | 2.463 (1) | Co(*l*)–S(*l*22) | 2.274 (2) | 2.285 (2) |
| Cu(*l*)–S(*l*11) | 2.431 (2) | 2.390 (2) | Co(*l*)–S(*l*31) | 2.258 (2) | 2.270 (2) |
| Cu(*l*)–S(*l*32) | 2.393 (2) | 2.399 (2) | Co(*l*)–S(*l*32) | 2.299 (2) | 2.307 (2) |
| Cu(*l*)···Co(*l*) | 3.330 (1) | 3.286 (1) | | | |
| | | Angles (deg) | | | |
| S(*l*11)–Co(*l*)–S(*l*12) | 76.86 (6) | 76.39 (7) | S(*l*31)–Co(*l*)–S(*l*32) | 76.72 (7) | 76.23 (6) |
| S(*l*11)–Co(*l*)–S(*l*21) | 97.09 (6) | 94.22 (7) | Cu(*l*)–S(*l*11)–Co(*l*) | 90.01 (6) | 88.90 (6) |
| S(*l*11)–Co(*l*)–S(*l*22) | 168.79 (11) | 164.62 (7) | Cu(*l*)–S(*l*11)–C(*l*11) | 91.0 (2) | 94.6 (2) |
| S(*l*11)–Co(*l*)–S(*l*31) | 92.35 (6) | 95.92 (7) | Co(*l*)–S(*l*11)–C(*l*11) | 85.6 (2) | 86.0 (2) |
| S(*l*11)–Co(*l*)–S(*l*32) | 92.58 (7) | 93.46 (7) | Cu(*l*)–S(*l*32)–Co(*l*) | 90.40 (6) | 88.57 (6) |
| S(*l*12)–Co(*l*)–S(*l*21) | 95.96 (7) | 97.40 (7) | Cu(*l*)–S(*l*32)–C(*l*31) | 96.2 (2) | 91.7 (2) |
| S(*l*12)–Co(*l*)–S(*l*22) | 94.27 (6) | 92.25 (7) | Co(*l*)–S(*l*32)–C(*l*31) | 84.9 (3) | 85.5 (2) |
| S(*l*12)–Co(*l*)–S(*l*31) | 167.18 (12) | 168.03 (11) | S(*l*11)–Cu(*l*)–Br(*l*) | 118.92 (6) | 116.40 (5) |
| S(*l*12)–Co(*l*)–S(*l*32) | 96.63 (7) | 94.89 (6) | S(*l*11)–Cu(*l*)–Br(*l*′) | 113.07 (5) | 110.33 (6) |
| S(*l*21)–Co(*l*)–S(*l*22) | 76.78 (7) | 76.77 (7) | S(*l*32)–Cu(*l*)–Br(*l*) | 114.81 (5) | 112.98 (6) |
| S(*l*21)–Co(*l*)–S(*l*31) | 92.18 (7) | 92.25 (7) | S(*l*32)–Cu(*l*)–Br(*l*′) | 113.61 (5) | 116.31 (5) |
| S(*l*21)–Co(*l*)–S(*l*32) | 165.59 (9) | 166.76 (6) | S(*l*11)–Cu(*l*)–S(*l*32) | 86.50 (6) | 88.98 (7) |
| S(*l*22)–Co(*l*)–S(*l*32) | 97.23 (6) | 96.86 (7) | Br(*l*)–Cu(*l*)–Br(*l*′) | 108.68 (5) | 110.50 (5) |
| S(*l*22)–Co(*l*)–S(*l*32) | 95.29 (6) | 97.88 (7) | Cu(*l*)–Br(*l*)–Cu(*l*′) | 66.50 (4) | 66.73 (4) |

3-fold axis) vary between 39.5 and 53.7°, the mean value being 44.9°; in consequence, in an idealized molecule the two pseudo-3-fold axes of each Co(dtc)$_3$ molecule will have a mutual torsion angle not differing significantly from the (theoretically nonobligatory) 90° about the Co···Co line.

(c) In consequence of (a), the shortest S···S contacts (between those sulfur atoms coordinated to the copper atoms) across the CuBr$_2$Cu moiety are grossly disparate. S(132)···S(211) is 4.844 (3) Å while S(111)···S(232) is 7.091 (3) Å.

We now comment on the geometries of the individual moieties: Seemingly, coordination of the CuBr$_2$Cu unit, by wedging between the upper and lower trigonal planes, has only a minor effect on the geometries of the Co(dtc)$_3$ "molecules". In tris(diethyldithiocarbamato)cobalt(III)[7] the mean Co–S distance is 2.25$_8$ Å; in the unsubstituted parent tris(dithiocarbamato)cobalt(III)[8] it is 2.27$_5$ Å. Although the range in the present complex is quite large (2.258 (2)–2.307 (2) Å), the mean 2.28$_1$ Å is comparable with the value found for the unsubstituted parent, a value not surprising in view of the comparable crystal field strengths of the ligands in these two cases.[9] For the sulfur atoms coordinated to copper as well as to cobalt, the mean value is 2.29$_6$ Å, indicating a significant lengthening of these cobalt–sulfur bonds relative to the remainder (mean 2.27$_2$ Å). Octahedral twist angles, $\theta$, of the two Co(dtc)$_3$ molecules are 22.6 and 22.2°, cf. 22.6 and 21.8°, respectively, for the cobalt(III) complexes of the parent and diethyl-substituted ligand.[10] Intramolecular nonbonded S···S contacts are relatively even (range 3.266 (2)–3.375 (2) Å, those involved in coordination to the copper atom lying in the middle of the range (3.306 (2), 3.356 (2) Å) rather than at either extreme. Dihedral angles between the S$_3$ planes defined by the upper and lower faces of the coordination sphere about the pseudo-3-fold axis are 2.3 and 2.5° for the two molecules, while the two dihedral angles of those faces to the associated CuBr$_2$ planes are 42.3 and 62.3° (molecule 1) and 60.5 and 48.7° (molecule 2). Deviations of the cobalt atoms from planes defined by the S$_2$CNC$_2$ ligand skeletons are 0.048, 0.169, and 0.116 Å (molecule 1) and 0.176,

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*Inorg. Chem.* **1985**, *24*, 385-397

0.092, and 0.154 Å (molecule 2). Peripheral C(3,4) atom deviations vary between 0.00 and 0.50 Å, depending on whether the pyrrolidine ring has 2-fold or "envelope" symmetry.

In the absence of a substantial array of complexes of the type $L_{(2)}CuBr_2CuL_{(2)}$, for comparative discussion of the $Cu_2Br_2$ moiety, a useful base line structural type is that of $[Cu(NH_3)_4](CuBr)_2$.[11] This, like its chloride analogue, crystallizes in space group $I4/mmm$ and contains infinite $-CuBr_2CuBr_2CuBr_2Cu-$ chains, with the copper atoms located on Wyckoff position *d* at $(0, {}^1/_2, {}^1/_4)$ etc. with symmetry $\bar{4}m2$ and separated from their congeners within the polymer at $(0, {}^1/_2, {}^3/_4)$ etc. by $c/2$ (=2.857 (4) (bromide), 2.734 (4) Å (chloride)), while the bromide at $(x, {}^1/_2, 0)$ (Wyckoff *j*) is separated by $2x = 0.3968$ (0.3774 (chloride) $a = 4.12$ (3.85 Å chloride)). These latter values are slightly greater than the usual van der Waals estimates of ~3.9 and 3.6 Å, respectively,[12] while the former may be compared with the interatomic separation in the metal of 2.56 Å.[13] Cu···Cu in the present complex is nearer the value observed in the metal, being 2.697 (2) Å, while Br···Br, 4.013 Å, is also shorter than in the anion polymer. The shortening of both of these distances simultaneously in the present complex may be attributed to relatively weak copper···sulfur bonding, effectively diminishing the coordination number of the copper atom. The copper–sulfur distance in copper(I) carbodithioate complexes has only been established for the tetrameric $[Cu(S_2CNEt_2)]_4$ species[14] in which it ranges from 2.246 (7) to 2.290 (6) Å. Values obtained for a variety of similar but not truly parallel interspecies interactions such as the trigonal $S_2$:::CuBr array in $(t\text{-BuNC})_4Mo(\pm\text{-}t\text{-BuS})_2CuBr$ (2.233 (3)–2.244 (3) Å[15]), $[[(\text{piperidine } N\text{-oxide}(1-))_2Mo(\pm\text{-S})_2Cu(\pm\text{-Cl})]_2]$ (2.266 (1) Å)[4] (tetrahedral Cu), $[Cu(S_2CNC_5H_{10})_2](CuBr)_4$, (2.3163 (9) Å), and$[Cu(S_2CNC_5H_{10})_2](CuBr)_6$ (2.284 (4), 2.305 (2), 2.476 (3) Å)[16] all tend to indicate the norm for a copper(I)···sulfur interaction in the context of trigonal or tetrahedral environments to be considerably less than the present values that range from 2.390 (2) to 2.431 (2) Å. The weakness of this interaction is corroborated by the relatively small perturbations noted above on the geometry of the $Co(dtc)_3$ molecule. Accordingly, the geometry of the $Cu_2Br_2$ species may perhaps be regarded as more akin to that of a matrix-isolated dimer.

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**Registry No.** $(Co(dtc)_3)CuBr_2Cu(Co(dtc)_3)$, 93984-80-6.

**Supplementary Material Available:** Listings of thermal parameters, hydrogen parameters, least-squares planes, ligand geometries, and observed and calculated structure factor amplitudes (23 pages). Ordering information is given on any current masthead page.

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# Directed, Intramolecular Electron Transfer in Mixed-Valence Dimers

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One-electron oxidation of the dimers $[(dpte)_2ClRu^{II}(L)Ru^{II}Cl(bpy)_2]^{2+}$ (dpte = $PhSCH_2CH_2SPh$; bpy = 2,2′-bipyridine; L = 4,4′-bipyridine (4,4′-bpy), *trans*-1,2-bis(4-pyridyl)ethylene (bpe), 1,2-bis(4-pyridyl)ethane (bpa)) gives the corresponding mixed-valence dimers $[(dpte)_2ClRu^{II}(L)Ru^{III}Cl(bpy)_2]^{3+}$. In the mixed-valence dimers, Ru(II) → Ru(III) intervalence-transfer (IT) bands are observed. Photolysis into either the $\pi^*(bpy) \leftarrow d\pi(Ru^{II}Cl(bpy)_2)$ chromophore for the Ru(II)–Ru(II) dimers or the $\pi^*(L) \leftarrow d\pi(Ru^{II}Cl(dpte)_2)$ chromophore for the mixed-valence dimers results in population of the bpy-based, $^3$MLCT excited state $(-Ru^{III}Cl(bpy^{-}\cdot)(bpy)^*)$ as shown by comparisons between room-temperature emission and low-temperature (220–280 K) transient absorption properties of the dimers and the related monomers $[(bpy)_2ClRu(L)]^+$. The appearance of the $^3$MLCT-bpy-based emission in the mixed-valence dimers shows that following $\pi^*(L) \leftarrow d\pi(Ru^{II}Cl(dpte)_2)$ excitation, ligand to ligand electron transfer, $[(dpte)_2ClRu^{III}(L^{-}\cdot)Ru^{III}Cl(bpy)_2]^{3+*} \rightarrow [(dpte)_2ClRu^{III}(L)Ru^{III}Cl(bpy^{-}\cdot)(bpy)]^{3+*}$, occurs and is competitive with excited-state nonradiative decay by ligand to metal electron transfer, $[(dpte)_2ClRu^{II}(L)Ru^{III}Cl(bpy)_2]^{3+} \leftarrow [(dpte)_2ClRu^{III}(L^{-}\cdot)Ru^{III}Cl(bpy)_2]^{3+*} \rightarrow [(dpte)_2ClRu^{III}(L)Ru^{II}Cl(bpy)_2]^{3+}$. Because of the relatively long lifetime of the $^3$MLCT-bpy state, it is not possible to observe relaxation of the high-energy, mixed-valence isomer to the ground state, $[(dpte)_2ClRu^{II}(L)Ru^{III}Cl(bpy)_2]^{3+} \rightarrow [(dpte)_2ClRu^{III}(L)Ru^{II}Cl(bpy)_2]^{3+}$, following nonradiative decay of $^3$MLCT-bpy. For the pentaammine Ru(II) dimers $[(NH_3)_5Ru^{II}(L)Ru^{II}Cl(bpy)_2]^{3+}$ (L = bpe, 4,4′-bpy), excitation into the $\pi^*(bpy) \leftarrow d\pi(Ru^{II})$ chromophore does not lead to emission or transient decay from the $^3$MLCT-bpy excited state apparently because of intramolecular energy transfer to lower lying, relatively short-lived $(NH_3)_5Ru^{III}$ $(L^{-}\cdot)$-based MLCT states. The $^3$MLCT-bpy excited state is also not observed following $\pi^*(bpy) \leftarrow d\pi(Ru^{II})$ excitation in the mixed-valence dimers $[(NH_3)_5Ru^{III}(L)Ru^{II}Cl(bpy)_2]^{4+}$ (L = 4,4′-bpy, bpe) either because of intramolecular quenching by Ru(III) or perhaps because of population of short-lived MLCT states based on the bridging ligand, $(NH_3)_5Ru^{III}(L^{-}\cdot)-$.

The nature and extent of the interaction between different chromophores in a single molecule or between a chromophore and a potential quencher has been and remains an area of active research in organic photochemistry. Many "bichromophoric" molecules have been synthesized and investigated from both the photochemical and photophysical points of view.[1] Established processes in such molecules include intramolecularly sensitized emission, photochemistry, and nonradiative decay by intramo-

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