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Structural Characterization of Bis[dibromo(*N*,*N*-dimethylethylenediamine)copper(II)] and Bis[dichloro(*N*,*N*-dimethylethylenediamine)copper(II)], $[Cu(dmen)Br_2]_2$ and $[Cu(dmen)Cl_2]_2$

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The crystal and molecular structures of bis[dibromo(*N*,*N*-dimethylethylenediamine)copper(II)], $Cu_2C_8H_{24}N_4Br_4$, $[Cu(dmen)Br_2]_2$, and bis[dichloro(*N*,*N*-dimethylethylenediamine)copper(II)], $Cu_2C_8H_{24}N_4Cl_4$, $[Cu(dmen)Cl_2]_2$, have been determined by three-dimensional x-ray diffraction using counter data. The complexes are isomorphous, each crystallizing with four formula units per cell in the orthorhombic space group *Pbca*. The cell constants for the dibromo complex are $a = 9.990$ (5), $b = 8.795$ (3), and $c = 20.828$ (14) Å, with observed and calculated densities of 2.25 and 2.261 g cm^{-3}, respectively. The corresponding values for the dichloro complex are $a = 9.765$ (9), $b = 8.518$ (6), $c = 20.767$ (20) Å and $d_{obsd} = 1.70$, $d_{calcd} = 1.712$ g cm^{-3}. The structures have been refined using full-matrix least-squares techniques, the final value of the conventional *R* factor (on *F*) being 0.043 for both structures based on 1412 data for the dibromo complex and 1360 data for the dichloro complex. The structures consist of dihalogen-bridged dimers, the out-of-plane Cu–Br′ and Cu–Cl′ distances being 2.868 (2) and 2.734 (3) Å, respectively, and the Cu–Cu′ separations being 3.570 (3) and 3.458 (3) Å for the dibromo and dichloro complexes, respectively. The geometry at the copper centers is tetragonal pyramidal, with two halogens and two nitrogen atoms in the base and the bridging halogen atom at the apex. The bridging Cu–Br(2)–Cu′ and Cu–Cl(2)–Cu′ angles are 83.71 (5) and 86.13 (8)°, respectively. The bridging unit of the dibromo complex is much more compact than that observed in other tetragonal-pyramidal dibromo-bridged copper(II) dimers, but both it and that of the dichloro complex are similar to that observed in $[Cu(DMG)Cl_2]_2$.

Introduction

There has been considerable recent research activity aimed at the correlation of the structural and magnetic properties of dimeric copper(II) complexes,[1] with major emphasis placed on systems in which the bridging atoms are oxygen atoms.[1-4] More recently, attention has also been focused on the dihalogen-bridged systems of general formulation $CuLX_2$ (where L is bidentate) or CuA_2X_2 (where A is unidentate), and dimeric structures have now been reported in which the geometry at copper is tetrahedral,[5,6] trigonal bipyramidal,[7-9] and tetragonal pyramidal;[10-15] a number of tetrameric[16] and polymeric materials of this general formulation have also been documented.[17-25]

The number of structural data available for any given dimeric structural type, however, remains too small to allow meaningful correlations; thus, for example, while more data are available for the out-of-plane tetragonal-pyramidal dimers than for any other class, there are only four structures of dichloro-bridged systems[10-13] and only two of dibromo-bridged complexes.[14,15] The discovery[13,15] that the *N*,*N*,*N′*,*N′*-tetramethylethylenediamine complexes $[Cu(tmen)X_2]_2$ were of this type while the corresponding tetraethyl complex $Cu(teen)Cl_2$ was not[26] suggested to us that the symmetric and unsymmetric dimethyl complexes were worthy of our attention. The preparations, space groups, and cell constants of the 1,1 unsymmetrical complexes with $CuBr_2$ and $CuCl_2$, dibromo- and dichloro(*N*,*N*-dimethylethylenediamine)copper(II), were recently reported by Näsänen et al.[27] We here report the complete three-dimensional crystal structures of these two complexes.

Table I. Positional Parameters ($\times 10^4$) for $[Cu(dmen)Br_2]_2$

Atom	*x*	*y*	*z*
Cu	577 (1)	577 (1)	774 (0)
Br(1)	905 (1)	1916 (1)	1216 (0)
Br(2)	1958 (1)	−2 (1)	−176 (0)
N(1)	−238 (6)	−1459 (6)	1608 (3)
N(2)	512 (7)	−2718 (6)	463 (3)
C(1)	−1344 (10)	−622 (10)	1898 (4)
C(2)	839 (9)	−1532 (9)	2094 (4)
C(3)	−770 (9)	−2962 (9)	1428 (5)
C(4)	214 (9)	−3784 (8)	980 (5)
H(41)[a]	−300	−4800	850
H(42)	800	−3850	1300
H(31)	−975	−3567	1767
H(32)	−1750	−3087	1272
H(11)	−2073	−730	1577
H(12)	−1216	204	1727
H(13)	−1780	−1065	2336
H(21)	1638	−2124	1916
H(22)	1000	−300	1950
H(23)	1100	−1200	2600
H(N(1))	923	−3035	91
H(N(2))	−439	−2707	173

[a] Hydrogen atom parameters were not refined.

Experimental Section

Bis[dibromo(*N*,*N*-dimethylethylenediamine)copper(II)]. A sample of the compound was prepared by the method of Näsänen et al.[27] and dark green crystals were grown from a methanol solution. A suitable crystal measuring 0.009 × 0.047 × 0.041 cm in the [001], [110] and $[1\bar{1}0]$ directions was used for space group assignment and intensity data collection. Weissenberg and precession photographs taken with Cu Kα and Mo Kα radiations indicated systematic absences of *k* odd for 0*kl*, *l* odd for *h*0*l*, and *h* odd for *hk*0 reflections which indicated the space group *Pbca* of the orthorhombic system. This is in agreement with results reported previously.[27] The cell constants and their standard deviations determined by the least-squares procedure of Busing and Levy[28] on 12 carefully centered reflections are $a = 9.990$ (5), $b = 8.795$ (3), and $c = 20.828$ (14) Å. These values are in excellent

Table II. Anisotropic Thermal Parameters ($\times 10^4$) (in Å^2) for $[Cu(dmen)Br_2]_2$[a]

Atom	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
Cu	379 (5)	271 (4)	327 (5)	−27 (3)	41 (4)	−9 (3)
Br(1)	679 (6)	358 (4)	593 (6)	−95 (3)	53 (5)	−138 (4)
Br(2)	345 (4)	476 (4)	379 (4)	−23 (3)	35 (3)	30 (3)
N(1)	421 (40)	461 (32)	376 (36)	−51 (25)	7 (29)	31 (26)
N(2)	577 (41)	329 (28)	552 (41)	22 (27)	61 (37)	−17 (27)
C(1)	572 (59)	710 (53)	576 (58)	86 (43)	195 (49)	55 (49)
C(2)	626 (60)	671 (46)	354 (43)	18 (40)	−139 (44)	64 (37)
C(3)	531 (56)	535 (42)	639 (57)	−229 (38)	−10 (47)	194 (42)
C(4)	603 (57)	318 (35)	659 (60)	22 (35)	−43 (48)	71 (37)

[a] In this and subsequent tables, the form of the anisotropic thermal ellipsoid is $\exp[-2\pi^2(U_{11}h^2a^{*2} + U_{22}k^2b^{*2} + U_{33}l^2c^{*2} + 2U_{12}hka^*b^* + 2U_{13}hla^*c^* + 2U_{23}klb^*c^*)]$.

agreement with those reported by Näsänen et al.[27] The measured density of the crystals by flotation in a mixture of benzene and bromoform is 2.25 g cm^{-3} and the calculated density assuming four dimeric molecules per unit cell is 2.261 g cm^{-3}. Thus, dimeric units in the cell are constrained to lie on an inversion center.

Diffraction data were collected using a Picker four-circle automatic diffractometer; the wavelength was assumed to be (Mo Kα) 0.7093 Å. The crystal was mounted on a glass fiber parallel to the *a* axis and in this orientation intensity data were collected at a takeoff angle of 1.6°; at this angle the peak intensity of a typical strong reflection was approximately 90% of the maximum value as a function of takeoff angle. A total of 2532 independent reflections were examined using Mo Kα radiation by the θ–2θ scan technique in the range $2° \leq 2\theta$ (Mo Kα) $\leq 55°$ at a scan rate of 1° min^{-1}. There were few intensities greater than background at values of $2\theta > 55°$. To allow for the presence of both Kα_1 and Kα_2 radiations, the scan range for each reflection was from 0.6° below the calculated Kα_2 position to 0.6° above the calculated Kα_2 position. Stationary-counter, stationary-crystal background counts of 10 s were taken at each end of the scan. Throughout the data collection the intensities of three standard reflections were measured every 100 reflections. All three reference reflections showed approximately a 7% decline in intensity during the data collection, and a linear correction was applied to account for this observed loss in intensity as a function of x-ray exposure.[29]

Data processing was carried out as described by Corfield et al.[30] After correction for background, the intensities were assigned standard deviations according to the formula $\sigma(I) = (C + 0.25(t_s/t_b)^2(B_H + B_L) + (pI)^2)^{1/2}$ and the value of p was chosen as 0.04. This term in the expression prevents extremely high weight being given to very large reflections.[31] The values I and $\sigma(I)$ were corrected for Lorentz–polarization effects and for absorption.[32] The absorption coefficient for this compound for Mo Kα radiation is 109.7 cm^{-1}, and for the sample chosen the transmission coefficients were found to range from 0.05 to 0.41. Of the 2532 reflections collected, 1412 with $F^2 > 3\sigma(F^2)$ were considered observed and only these observed reflections were used in subsequent calculations.

Bis[dichloro(*N*,*N*-dimethylethylenediamine)copper(II)]. A sample of the compound was prepared by the method of Näsänen et al.[27] and blue crystals were grown from a methanol solution. Diffraction data were obtained from a crystal of morphology similar to that of the bromide salt with dimensions 0.014 × 0.057 × 0.052 cm in the [001], [110], and [$\bar{1}$10] directions. In view of the similar shapes of the two crystals and of the previously reported results,[27] the space group was believed to be the same as that for the dibromo complex, *Pbca*. The cell constants and their standard deviations determined by the least-squares procedure of Busing and Levy[28] on 12 carefully centered reflections are $a = 9.765$ (9), $b = 8.518$ (6), and $c = 20.767$ (20) Å. The density measured by flotation in a mixture of benzene and bromoform is 1.70 g cm^{-3} and the calculated density assuming four dimeric molecules per unit cell is 1.712 g cm^{-3}. These results are in good agreement with those of Näsänen et al.[27]

Intensity data were collected using Mo Kα radiation with the crystal mounted approximately parallel to the *a* axis using a takeoff angle of 2.8°. A total of 2391 independent reflections were examined in the range 2θ(Mo Kα) $\leq 55°$ at a scan rate of 1° min^{-1}. The presence of both Kα_1 and Kα_2 radiations was again allowed for by using a scan range from 0.8° below the calculated Kα_1 position to 0.8° above the Kα_2 position. Stationary-counter, stationary-crystal background counts of 10 s were taken at each end of the scan. The three reference reflections examined every 100 reflections were again found to undergo a drop in intensity of about 6%; a linear correction was applied.

Table III. Positional Parameters ($\times 10^4$) for $[Cu(dmen)Cl_2]_2$

Atom	*x*	*y*	*z*
Cu	641 (1)	−566 (1)	741 (0)
Cl(1)	911 (2)	1833 (2)	1179 (1)
Cl(2)	1854 (1)	85 (2)	−176 (1)
N(1)	−146 (6)	−1543 (6)	1577 (3)
N(2)	578 (5)	−2762 (5)	413 (3)
C(1)	−1311 (10)	−686 (12)	1857 (5)
C(2)	906 (8)	−1568 (10)	2071 (4)
C(3)	−670 (10)	−3087 (10)	1391 (4)
C(4)	195 (8)	−3864 (8)	924 (5)
H(41)[a]	−300	−4800	850
H(42)	800	−3850	1300
H(32)	−1750	−3100	1250
H(31)	−1000	−3550	1750
H(11)	−2006	−654	1537
H(12)	−1198	210	1756
H(13)	−1717	−1086	2290
H(21)	1749	−2224	1904
H(22)	1119	−476	2042
H(23)	1189	−1311	2524
H(N(1))	100	−2798	65
H(N(2))	1379	−3080	229

[a] Hydrogen atom parameters were not varied.

The data were processed as described above and corrected for Lorentz–polarization and absorption effects.[32] The absorption coefficient for this compound for Mo Kα radiation is 30.84 cm^{-1} and for the sample chosen the transmission coefficients were found to range from 0.26 to 0.71. Of the 2391 reflections collected, 1360 with $F^2 > 3\sigma(F^2)$ were considered observed, and only these reflections were used in subsequent calculations.

Solution and Refinement of Structure

All least-squares refinements in these analyses were carried out on F, the function minimized being $\sum w(|F_o| - |F_c|)^2$; the weights w were taken as $4F_o^2/\sigma^2(F_o^2)$. In all calculations of F_c the atomic scattering factors for all heavy atoms were taken from ref 33a and those for hydrogen were taken from Stewart, Davidson, and Simpson.[34] The effects of the anomalous dispersion of Cu, Br, and Cl were included in calculations of F_c,[35] the values of $\Delta f'$ and $\Delta f''$ being taken from ref 33b. The unweighted and weighted residuals are defined as $R_1 = \sum||F_o| - |F_c||/\sum|F_o|$ and $R_2 = [\sum w(|F_o| - |F_c|)^2/\sum w(F_o)^2]^{1/2}$.

Bis[dibromo(*N*,*N*-dimethylethylenediamine)copper(II)]. The positions of the Cu and Br atoms were determined from a three-dimensional Patterson function, and all remaining nonhydrogen atoms were located from a three-dimensional Fourier map phased on these heavy-atom positions. The hydrogen atoms could be located in a Fourier map phased on the anisotropic refinement of all nonhydrogen atoms; since attempts to refine these hydrogen atom parameters were unsuccessful, they were placed in the positions determined from the Fourier map and not varied in the least-squares refinement. All hydrogen atoms were assigned isotropic thermal parameters of 7.0 Å^2.

In the final cycle of refinement there were 83 varied parameters and 1412 reflections, which gives a reflection to parameter ratio of 17:1. In the last cycle of least-squares refinement no parameter shifted by more than 0.5 esd, which indicated that refinement had converged. The final R_1 and R_2 values were found to be 0.043 and 0.052 and the error in an observation of unit weight was observed to be 1.66. The value of R_2 showed no dependence on $\sin\theta$ or on $|F_o|$, which

Table IV. Anisotropic Thermal Parameters ($\times 10^4$) (in Å^2) for $[Cu(dmen)Cl_2]_2$

Atom	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
Cu	406 (4)	301 (4)	428 (4)	−39 (3)	−7 (3)	−5 (3)
Cl(1)	808 (12)	389 (8)	824 (13)	−78 (8)	−55 (10)	−161 (8)
Cl(2)	371 (7)	601 (9)	534 (10)	−68 (6)	6 (7)	103 (7)
N(1)	671 (35)	567 (30)	467 (31)	−113 (26)	−27 (27)	29 (25)
N(2)	562 (32)	388 (24)	605 (33)	57 (22)	14 (25)	−72 (23)
C(1)	696 (54)	1524 (91)	778 (60)	81 (56)	225 (50)	270 (60)
C(2)	855 (56)	898 (55)	493 (42)	123 (44)	−189 (38)	37 (40)
C(3)	1196 (75)	748 (51)	785 (57)	−405 (50)	228 (52)	44 (46)
C(4)	744 (49)	286 (29)	1283 (76)	−37 (33)	228 (51)	81 (38)

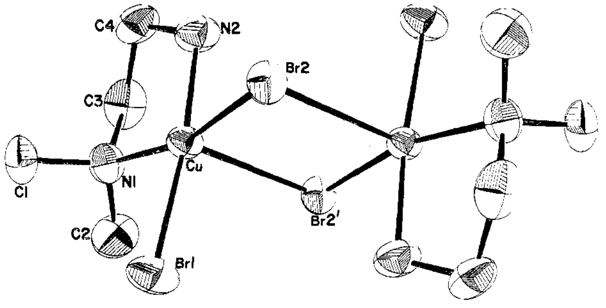

Figure 1. View of the $[Cu(dmen)X_2]_2$ dimeric unit. The figure shown is the dibromo complex (X = Br), but the dichloro complex is very similar. Hydrogen atoms have been omitted for clarity.

indicates that our assignment of $p = 0.04$ in the weighting scheme was essentially correct. Examination of the values of $|F_o|$ and $|F_c|$ in the later cycles of refinement for reflections with large F and low $\sin \theta$ indicated that the data needed a correction for secondary extinction. The application of a correction of the type described by Zachariasen[36] led to a value for the extinction coefficient of 7 (2) $\times 10^{-8}$.

A final difference Fourier map showed no peak greater than 0.4 e Å^{-3} except for some residual density up to 0.9 e Å^{-3} near the bromine atoms. This residual density is presumably due to some small error in our absorption correction, and is not wholly unexpected in view of the large value of μ for this compound. The positional and thermal parameters derived from the last cycle of least-squares refinement, along with their associated standard deviations as estimated from the inverse matrix, are presented in Tables I and II. A table of observed and calculated structure amplitudes is available.[37]

Bis[dichloro(*N*,*N*-dimethylethylenediamine)copper(II)]. An initial model in which the coordinates of all nonhydrogen atoms of the dibromo complex (with Cl replacing Br) were used in the first cycle of least squares with the data for the dichloro complex gave an R value of 0.064. The hydrogen atoms were located from a difference Fourier map phased on the anisotropic refinement of the nonhydrogen atoms. These hydrogen atoms would not refine satisfactorily and their positions were held constant in all remaining least-squares cycles. Isotropic thermal parameters of 7.0 Å^2 were assigned to the hydrogen atoms.

In the final cycle of refinement there were 83 varied parameters and 1360 reflections, and no parameter shifted by more than 0.7 esd. The final R_1 and R_2 values were found to be 0.043 and 0.068 with the error on an observation of unit weight being 2.49. No dependence of R_2 on $\sin \theta$ or $|F_o|$ was observed but again an extinction correction[36] was necessary and refined to a value of 2.3 (8) $\times 10^{-8}$. The final difference Fourier map showed only one peak greater than 0.5 e Å^{-3}, that of 0.9 e Å^{-3} close to Cl(1). The positional and thermal parameters, along with their associated standard deviations as estimated from the inverse matrix, are presented in Tables III and IV. A table of observed and calculated structure amplitudes is available.[37]

Description of the Structures

Both complexes consist of dimeric $[Cu(dmen)X_2]_2$ which are well separated from other dimers in the cell; a view of the dimer is given in Figure 1. The bridging Cu_2X_2 units are strictly planar, there being a crystallographic inversion center in the middle of dimer. The bond lengths and angles in the two dimers are compared in Tables V and VI, and the bridging geometries are compared in Figure 2. The geometry at the copper centers is tetragonal pyramidal, with N(1), N(2), X(1), and X(2) [X = Cl, Br] forming the base and X(2)′ occupying the apical site. The bridge is formed by atoms Cu, X(2), X(2)′, and Cu′, where atom X(2) is equatorial to Cu and apical to Cu′ and vice versa for atom X(2)′; the primed atoms are related to the reference atoms by inversion through the origin.

Table V. Internuclear Distances (Å) in $[Cu(dmen)X_2]_2$

Atoms	X = Br	X = Cl
Cu-Cu′	3.570 (3)	3.458 (3)
Cu-X(1)	2.401 (1)	2.253 (2)
Cu-X(2)	2.463 (2)	2.309 (2)
Cu-X(2)′	2.868 (2)	2.734 (3)
Cu-N(1)	2.070 (6)	2.074 (6)
Cu-N(2)	1.992 (5)	1.991 (5)
N(1)-C(1)	1.460 (11)	1.471 (11)
N(1)-C(2)	1.479 (10)	1.452 (9)
N(1)-C(3)	1.473 (9)	1.463 (10)
C(3)-C(4)	1.537 (13)	1.447 (12)
C(4)-N(2)	1.459 (10)	1.465 (12)

Table VI. Internuclear Angles (deg) in $[Cu(dmen)X_2]_2$

Atoms	X = Br	X = Cl
Cu-X(2)-Cu′	83.71 (5)	86.13 (8)
N(1)-Cu-N(2)	84.6 (2)	84.1 (2)
N(1)-Cu-X(1)	94.2 (2)	94.0 (2)
N(1)-Cu-X(2)	166.2 (2)	167.7 (2)
N(1)-Cu-X(2)′	94.8 (2)	95.1 (2)
N(2)-Cu-X(1)	172.9 (3)	173.6 (2)
N(2)-Cu-X(2)	87.2 (2)	87.7 (2)
N(2)-Cu-X(2)′	89.9 (2)	88.1 (1)
X(1)-Cu-X(2)	92.52 (4)	93.16 (8)
X(1)-Cu-X(2)′	97.19 (4)	98.15 (7)
X(2)-Cu-X(2)′	96.29 (5)	93.87 (8)
Cu-N(1)-C(1)	117.2 (5)	114.7 (5)
Cu-N(1)-C(2)	107.8 (5)	109.6 (5)
Cu-N(1)-C(3)	105.4 (5)	105.6 (4)
C(1)-N(1)-C(2)	106.8 (7)	106.0 (7)
C(1)-N(1)-C(3)	106.5 (6)	106.3 (7)
C(2)-N(1)-C(3)	113.4 (6)	114.9 (6)
Cu-N(2)-C(4)	112.0 (5)	111.2 (5)
N(1)-C(3)-C(4)	110.2 (6)	111.6 (7)
C(3)-C(4)-N(2)	106.0 (6)	110.0 (6)

Table VII. Bridging Geometry in Dibromo-Bridged Copper(II) Dimers

	$[Cu(pic)_2Br_2]_2$	$[Cu(tmen)Br_2]_2$	$[Cu(MAEP)Br_2]_2$	$[Cu(dmen)Br_2]_2$
Cu-Cu′, Å	4.926 (6)	4.20	3.803 (4)	3.570 (3)
Cu-Br′, Å	3.872 (5)	3.20	2.802 (4)	2.868 (2)
Cu-Br-Cu′, deg	100.4 (1)	95.6 (5)	92.14 (9)	83.71 (5)
Geometry at Cu	TP[a]	TP	TBP[b]	TP
Ref	14	15	9	This work

[a] Tetragonal pyramidal. [b] Trigonal bipyramidal.

$[Cu(dmen)Br_2]_2$. The equatorial Cu-Br distances are 2.401 (1) and 2.463 (2) Å, with the distance to the bridging atom appreciably longer than that to the terminal atom. The terminal distances can be compared with the values of 2.413 (3) and 2.40 Å found for terminal Cu-Br in the tetrago-

Table VIII. Bridging Geometry in Tetragonal-Pyramidal Dichloro-Bridged Copper(II) Dimers

	$[Cu(DMG)Cl_2]_2$	$[Cu(pic)_2Cl_2]_2$	$[Cu(tmen)Cl_2]_2$	$[Cu(9Me6MP)Cl_2]_2$	$[Cu(dmen)Cl_2]_2$
Cu-Cu′, Å	3.45	4.41	4.089 (4)	3.519 (1)	3.458 (3)
Cu-Cl′, Å	2.698	3.37	3.147 (4)	2.737 (1)	2.734 (3)
Cu-Cl-Cu′, deg	88.0	101.4	96.8 (1)	88.17	86.13 (8)
Ref	11	12	13	10	This work

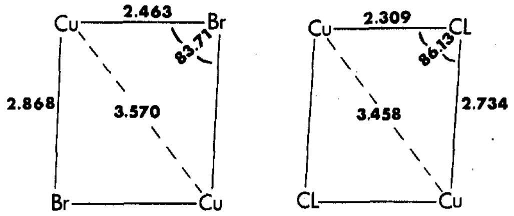

Figure 2. Comparison of the bridging geometries of $[Cu(dmen)Cl_2]_2$ and $[Cu(dmen)Br_2]_2$.

nal-pyramidal dimers $[Cu(pic)_2Br_2]_2$ (pic = 2-methylpyridine)[14] and $[Cu(tmen)Br_2]_2$,[15] respectively, and with the value of 2.400 (3) Å in the trigonal-bipyramidal dimer $[Cu(MAEP)Br_2]_2$ [MAEP = 2-(2-methylaminoethyl)pyridine].[9] Similarly, the Cu–Br(2) length is comparable to values of 2.426 (3), 2.42, and 2.468 (2) Å, respectively, found for the analogous bond in these three dimers.[9,14,15] It is evident from this comparison that these Cu–Br bond lengths in $[Cu(dmen)Br_2]_2$ are normal.

The out-of-plane Cu–Br(2)′ distance of 2.868 (2) Å is considerably shorter than the values of 3.872 (5) and 3.20 Å in $[Cu(pic)_2Br_2]$ and $[Cu(tmen)Br_2]_2$, respectively,[14,15] and is similar to the value of 2.802 (4) Å found for the equatorial bond in the trigonal-bipyramidal MAEP dimer.[9] The bridging Cu–Br(2)–Cu′ angle of 83.71 (5)° is much smaller than the obtuse values of 100.4 (1) and 95.6 (5)° found in the pic and tmen complexes. The consequence of these two features, of course, is that the Cu–Cu′ separation of 3.570 (3) Å is very much smaller than the values of 4.926 (6) and 4.20 Å in these other two dimers; this separation is also shorter than that of 3.803 (4) Å in the MAEP dimer and is, therefore, the shortest Cu–Cu′ separation yet reported for a dibromo-bridged copper(II) dimer. The bridging geometry found here is compared in detail with those of the other known dibromo-bridged copper(II) dimers in Table VII.

Despite the much stronger interaction found for this complex than for the other tetragonal-pyramidal dimers of this type, the magnetic-exchange parameter, *J*, for this complex is very small,[38] with a magnitude less than 10 cm^{-1}. This result comes about because the bridging angle of 83.71 (5)° precludes much orbital overlap, whereas the angle of 100.4° in the pic complex allows for slightly more overlap. In all of these out-of-plane dimers, of course, $|J|$ is relatively small because of this near orthogonality of the orbitals in the halves of the dimer.[3]

The Cu–N(1) distance of 2.070 (6) Å is within the range for such bonds observed in a large variety of structures in these laboratories, but the Cu–N(2) distance of 1.992 (5) Å is among the shortest bonds between copper and an amino nitrogen atom that we have observed.[39] The four basal atoms N(1), N(2), Br(1), and Br(2) are not quite coplanar, atoms Br(1) and N(2) lying 0.04 and 0.05 Å, respectively, above the best least-squares plane through the four atoms while atoms Br(2) and N(1) are 0.04 and 0.05 Å, respectively, below it. As is normal for tetragonal-pyramidal complexes,[12,40,41] the copper atom lies 0.18 Å above this plane in the direction of the apical atom Br(2)′. The bond lengths and angles associated with the substituted ethylenediamine rings are normal for complexes of this type;[13,15,26,42] the presence of the inversion center constrains each dimer to contain one δ and one λ ring. There is no compelling evidence for any intermolecular hydrogen bonding involving the protons on N(2).

$[Cu(dmen)Cl_2]_2$. The equatorial Cu–Cl distances are 2.253 (2) and 2.309 (2) Å; these distances are each approximately 0.15 Å less than the corresponding lengths in the dibromo complex, which is to be expected since the covalent radius of chlorine (0.99 Å) is 0.15 Å smaller than that of bromine (1.14 Å).[43] These distances are similar to the values found in other chloro-bridged copper(II) complexes.[5–8,10–13,16–20] As in the dibromo complex, the bridging geometry affords a stronger interaction than in most of the other tetragonal-pyramidal dimers, although it is comparable to that in the dimethylglyoxime complex[11] $[Cu(DMG)Cl_2]_2$ and the 6-mercaptopurine complex[10] $[Cu(9Me6MP)Cl_2]_2$. Thus, the out-of-plane Cu–Cl(2)′ distance, the Cu–Cu′ separation, and the bridging Cu–Cl(2)–Cu′ angle of 2.734 (3) Å, 3.458 (3) Å, and 86.13 (8)° are all very similar to the values of 2.698 Å, 3.45 Å, and 88.0°, respectively, found[11] in $[Cu(DMG)Cl_2]_2$ and those of 2.737 (1) Å, 3.519 (1) Å, and 88.17° in the 6-mercaptopurine complex;[10] as can be seen in Table VIII, these values are much smaller than those found[12,13] in the other tetragonal-pyramidal dichloro-bridged dimers, $[Cu(pic)_2Cl_2]_2$ and $[Cu(tmen)Cl_2]_2$.

On the basis of this bridging geometry, we would anticipate that the magnetic properties of $[Cu(dmen)Cl_2]_2$ are similar to those of $[Cu(DMG)Cl_2]_2$. In the latter, the ground state is reported[44] to be the triplet, with a $2J$ value (the triplet–singlet splitting) of only 6.3 cm^{-1}. Preliminary magnetic susceptibility measurements[38] are not inconsistent with this expectation, but more precise low temperature data will be needed before an accurate value for *J* can be obtained.

As was observed in the dibromo complex, the Cu–N(1) bond length of 2.074 (6) Å is significantly greater than the Cu–N(2) value of 1.991 (5) Å. This trend is not consistent with the known electron-donating capacity[45] of the methyl groups on N(1), which presumably leads to enhancement of the electron density at N(1) relative to that at N(2). The difference may, however, be due to the greater steric crowding at N(1), which brings about a small Cu–N(1)–C(3) chelate angle of 105.6 (4)° [vs. 111.2 (5)° at N(2)] and which could be relieved by a slight lengthening of the Cu–N(1) bond. The same effect is found in the dibromo complex [105.4 (5)° vs. 112.0 (5)°]. The four equatorial atoms N(1), N(2), Cl(1), and Cl(2) are again not coplanar, with Cl(1) and N(2) being 0.03 and 0.04 Å, respectively, above the least-squares plane through the four atoms while Cl(2) and N(1) are 0.03 and 0.04 Å, respectively, below it; the copper atom is 0.15 Å above this plane, toward the apical atom Cl(2)′. The geometry of the substituted ethylenediamine ligand is normal, with one δ and one λ conformer in each dimer.

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Registry No. $[Cu(dmen)Cl_2]_2$, 59493-10-6; $[Cu(dmen)Br_2]_2$, 59492-72-7.

Supplementary Material Available: Listings of structure factor amplitudes (16 pages). Ordering information is given on any current masthead page.

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Crystal and Molecular Structure of Di-μ-bromo-bis[dibromo(diethyl sulfoxide)nitrosylruthenium(II)]

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The crystal and molecular structures of di-μ-bromo-bis[dibromo(diethyl sulfoxide)nitrosylruthenium(II)], $[RuBr_3(NO)(Et_2SO)]_2$, have been determined from three-dimensional x-ray data obtained by counter methods. The compound crystallizes in the centrosymmetric space group $P\bar{1}$ of the triclinic system, with 1 formula unit in a unit cell of dimensions $a = 8.042$ (1) Å, $b = 11.020$ (2) Å, $c = 7.324$ (1) Å, $\alpha = 104.83$ (1)°, $\beta = 102.31$ (1)°, and $\gamma = 88.54$ (1)°. Full-matrix least-squares refinement of the structure has led to a final R value of 0.047 for the 1337 independent reflections having $F_o^2 > 3\sigma(F_o^2)$. The dimeric molecules consist of octahedrally coordinated ruthenium atoms sharing one edge through the two bridging bromine atoms, two coordinated to each ruthenium atom. Above and below this plane are nitrosyl and diethyl sulfoxide groups trans to each other on each ruthenium atom with a crystallographic center of symmetry imposed on the whole molecule. The nitrosyl ligand is linearly coordinated as expected for NO^+ complexes of Ru(II). This sulfoxide complex was formed from the $RuBr_3(NO)(Et_2S)_2$ complex dissolved in chloroform and exposed to sunlight. The oxidation was achieved by dioxygen dissolved in the chloroform assisted by the presence of ethanol. The diethyl sulfoxide ligand is coordinated to the Ru(II) atom through the oxygen atom.

Introduction

During the study of a series of complexes $RuX_3(NO)L_2$ (X = Cl, Br, I; L = Me_2S, PhMeS, Et_2S, PhEtS, Et_2Se, PhEtSe, $(n\text{-}Pr)_2S$, Ph-n-PrS)[1] it was observed that a chloroform solution of $RuBr_3(NO)(Et_2S)_2$ changed color from light yellow to dark red in sunlight. After a period of a few weeks a small quantity of dark red-brown crystals was separated from the solution. The infrared spectrum of these crystals contained a strong absorption at 920 cm^{-1} absent in the parent compound. This suggested the existence of a sulfoxide group bonded to the metal atom through its oxygen atom. The product of this ready conversion seemed best characterized by a crystal structure analysis. This analysis has confirmed the existence of sulfoxide ligands coordinated to ruthenium atoms. The source of the oxygen has also been investigated.

Experimental Section

Preparations. Nitric oxide was bubbled through an ethanol solution of $RuBr_3 \cdot 3H_2O$ for several hours, and then diethyl sulfide was added in slight excess. The solution was heated under reflux for 1 h. Crystals of $RuBr_3(NO)(Et_2S)_2$ formed as ethanol was removed in vacuo. A chloroform solution of $RuBr_3(NO)(Et_2S)_2$ was allowed to evaporate slowly over a period of a few weeks, while exposing the solution to sunlight. The mother liquor was poured off and the crystals obtained in low yield were dried in vacuo. Dark red-brown crystals, of empirical formula $RuBr_3(NO)(Et_2SO)$, formed.

Study of the Reaction. Exposure of chloroform solutions of $RuBr_3(NO)(Et_2S)_2$ to sunlight which first passed through color filters (Ilford) indicated that radiation within the wavelength range 380–480 nm was necessary.

The color change which was observed also corresponded to changes in the ^1H NMR and electronic spectra of the solution. The form of