Contribution from the Department of Chemistry,
The University of North Carolina, Chapel Hill, North Carolina 27514

Linear Metal Chain Complexes. Structural Characterization of Bis(pyridine-2-methylcarboxaldoximinato)platinum(II)

DANIEL W. PHELPS, WILLIAM F. LITTLE, and DEREK J. HODGSON*

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The crystal structure of bis(pyridine-2-methylcarboxaldoximinato)platinum(II), $Pt(C_7H_7N_2O)_2$, has been determined from three-dimensional x-ray data obtained using an automatic four-circle diffractometer and Mo Kα radiation. The material crystallizes in the space group *Pbcn* of the orthorhombic system with four formula units in a cell of dimensions $a = 12.410$ (8), $b = 15.763$ (10), and $c = 6.727$ (3) Å. The observed and calculated densities are 2.33 (2) and 2.35 g cm^{-3}, respectively. The structure has been refined by full-matrix least-squares methods using 803 independent intensities to a final value of the conventional R factor (on F) of 0.032. The structure consists of linear chains of planar $Pt(C_7H_7N_2O)_2$ units which are not normal to the Pt–Pt (or crystallographic c) axis. The planar units form a chain parallel to the crystallographic c axis, with a Pt–Pt separation of 3.363 Å ($c/2$). The coordination around the platinum centers is roughly square planar, the ligating atoms being the two nitrogen atoms from each of two ligands. The ligands in adjacent molecules in the chain are rotated relative to each other so that overlap between the pyridine rings is small. A powdered sample of the complex shows enhanced electrical conductivity which is of the same magnitude as that observed for Magnus green salt.

Introduction

Much interest in metal complex systems possessing direct interaction of transition metal ions has recently been demonstrated,[1] a large degree of this interest being brought about by the suggestion that metal complexes involving chains of metal atoms coordinated to highly polarizable ligiands have considerable potential as superconductors.[2]

Previous studies on planar d^8 systems indicate that the primary interatomic interactions are the metal–metal interactions resulting from the columnar stacking of the square-planar units.[3] Square-planar compounds such as the well-known Krogmann's salt, $K_2[Pt(CN)_4Br_{0.3}]\cdot 3.2H_2O$, and related nonstoichiometric mixed-valence platinum and iridium complexes show highly anisotropic electrical and optical properties in the solid state indicating one-dimensional interactions between the monomer units.[4] Although a large number of these stacked metal complexes have been synthesized, they suffer from the distinct disadvantage that the ligands involved allow little chemical modification. To circumvent this problem we have utilized the report of the synthesis[5] of bis(pyridine-2-carboxaldoximinato)platinum(II), which allows some chemical functionality in the ligand, to bring about the desired small changes in electronic environment at the metal centers. Earlier we reported the structure and conductivity properties of the parent molecule, bis(pyridine-2-carboxaldoximinato)platinum(II),[6] and we herein report the structural properties of the methyl derivative, bis(pyridine-2-methylcarboxaldoximinato)platinum(II). The purpose of this study was to determine the effects (if any) on the structure of the introduction of a substituent in the side chain of the ligand.

Experimental Section

The title compound was prepared by Dr. K. W. Nordquest and generously donated to us. Deep-red crystals suitable for structural analysis were obtained by slow cooling of a chloroform solution of the complex. The crystal used for space group assignment and intensity data collection measured 0.01 × 0.01 × 0.10 cm in the [110], [$\bar{1}$10], and [001] directions. Weissenberg and precession photographs taken with Cu Kα and Mo Kα radiations indicated systematic absences of k odd for $0kl$, l odd for $h0l$, $h + k$ odd for $hk0$, which would indicate the space group *Pbcn* ($D_{2h}{}^{14}$) of the orthorhombic system. Unit cell dimensions and their standard deviations determined by least-squares procedures[7] from diffractometer measurements of 12 reflections using Mo Kα_1 radiation (λ 0.7093 Å) are: $a = 12.410$ (8), $b = 15.763$ (10), $c = 6.727$ (3) Å. Assuming four molecules per unit cell the calculated density is 2.35 g cm^{-3}, in agreement with the measured density in bromoform and benzene of 2.33 (2) g cm^{-3}. Hence, with four formula units in the cell the platinum atom is required to lie on either an inversion center or a twofold axis of rotation.

Intensity data were taken with the crystal mounted on a glass fiber nearly parallel to the needle or c axis at a takeoff angle of 1.8°. The diffractometer was equipped with a graphite monochromator and a pulse height analyzer. A total of 2532 independent reflections was examined in the θ–2θ scan mode in the range $2° < 2\theta(\text{Mo}) < 60°$ at a scan rate of 1.0° min^{-1}. The scan range was from 0.85° below the calculated Kα_1 peak position to 0.85° above the calculated Kα_2 peak position and stationary-counter, stationary-crystal background counts of 10 s were taken at each end of the scan. During the data collection the intensities of three standard reflections were measured after every 100 reflections. There was no observed decrease in intensity of these reference reflections, indicating crystal and electronic stability during the data collection.

Data processing was carried out as described by Corfield et al.[8] After correction for background the intensities were assigned standard deviations according to the formula $\sigma(I) = [C + 0.25(t_s/t_b)^2(B_H + B_L) + p^2I^2]^{1/2}$, where C is the total counts, t_s and t_b are the scan time and background time, respectively, B_H and B_L are the background counts after and before the 2θ scan, I is the intensity of the peak, and p is an empirical correction term with a chosen value of 0.04. The intensities and their standard deviations were corrected for Lorentz–polarization effects and for absorption.[9] The absorption coefficient[10] for this compound for Mo Kα radiation is 112.4 cm^{-1}, and for the sample chosen the transmission coefficients were found to range from 0.30 to 0.47.

Solution and Refinement of the Structure. The structure was solved with standard Fourier and least-squares techniques. The platinum atom was deduced to be on the inversion center rather than on the twofold axis because data with l odd were uniformly weak. A Fourier map phased on the platinum atom at the origin of the cell with symmetry $\bar{1}$ revealed all remaining nonhydrogen atoms in general positions in the cell.

All least-squares refinements in this analysis were carried out on F, the function minimized being $\Sigma w(|F_o| - |F_c|)^2$ and the weights w being taken as $4F_o{}^2/\sigma^2(F_o{}^2)$. In all calculations of F_c, the atomic scattering factor for Pt was taken from Cromer and Waber,[11] that for H was taken from Stewart, Davidson, and Simpson,[12] and those for C, O, and N were taken from Ibers.[13] The effects of the anomalous dispersion of platinum were included in calculations of F_c,[14] the values of $\Delta f'$ and $\Delta f''$ for Pt being taken from the tabulation of Cromer.[15] The weighted and unweighted residuals are defined as $R_1 = \Sigma\|F_o| - |F_c\|/\Sigma|F_o|$ and $R_2 = [\Sigma w(|F_o| - |F_c|)^2/\Sigma w(F_o)^2]^{1/2}$.

The ring hydrogen atoms could be located from a difference Fourier map based on the anisotropic refinement of all ten nonhydrogen atoms. These atoms were, therefore, included in subsequent least-squares calculations, their positions being calculated on the basis of planar geometry in the ring and C–H distances of 0.95 Å; each hydrogen atom was assigned an isotropic thermal parameter of 5.0 Å^2, and no hydrogen atom parameter was varied. The methyl hydrogen atoms could not be located with any degree of certainty, obviously because

Table I. Positional Parameters (×10^4) for $[Pt(C_7H_7N_2O)_2]$

Atom	x	y	z
Pt	0	0	0
N(1)	1583 (7)	253 (6)	352 (9)
C(1)	1833 (8)	1092 (6)	325 (7)
C(2)	2884 (9)	1340 (7)	546 (16)
C(3)	3672 (8)	756 (9)	805 (16)
C(4)	3410 (9)	−78 (7)	838 (20)
C(5)	2358 (9)	−303 (8)	577 (15)
C(6)	936 (9)	1671 (6)	150 (14)
C(7)	1020 (9)	2618 (5)	187 (16)
N(2)	−3 (7)	1288 (6)	1 (10)
O(1)	−870 (6)	1736 (4)	−180 (10)
HC(2)[a]	3062	1910	545
HC(3)	4411	933	944
HC(4)	3937	−495	1019
HC(5)	2186	−884	533

[a] Hydrogen atom parameters were not varied.

Table II. Thermal Parameters for $[Pt(C_7H_7N_2O)_2]$[a]

	β_{11}[b] or B	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
Pt	470 (4)	211 (2)	1181 (11)	−1 (3)	88 (7)	11 (4)
N(1)	62 (6)	32 (3)	72 (20)	−6 (4)	14 (7)	−4 (5)
C(1)	63 (7)	31 (4)	45 (26)	−3 (5)	18 (9)	−8 (6)
C(2)	80 (9)	43 (6)	155 (25)	−17 (6)	25 (13)	−11 (9)
C(3)	47 (7)	56 (6)	216 (33)	−6 (6)	20 (13)	−4 (13)
C(4)	54 (7)	46 (6)	201 (28)	9 (6)	2 (12)	−12 (11)
C(5)	52 (8)	36 (4)	129 (19)	3 (5)	13 (11)	−10 (9)
C(6)	62 (7)	31 (4)	131 (23)	−12 (4)	2 (11)	12 (8)
C(7)	86 (9)	18 (3)	267 (33)	−9 (4)	−4 (14)	10 (8)
N(2)	71 (6)	29 (3)	172 (18)	15 (5)	7 (2)	4 (8)
O(1)	68 (6)	25 (3)	303 (25)	3 (3)	4 (10)	3 (6)
HC(2)	5.0					
HC(3)	5.0					
HC(4)	5.0					
HC(5)	5.0					

[a] Anisotropic thermal parameters for Pt are ×10^5 and those for all other nonhydrogen atoms are ×10^4. [b] The form of the anisotropic thermal ellipsoid is $\exp[-(\beta_{11}h^2 + \beta_{22}k^2 + \beta_{33}l^2 + 2\beta_{12}hk + 2\beta_{13}hl + 2\beta_{23}kl)]$.

of their potentially free rotation about the C(6)–C(7) bond, and were omitted from the refinement.

Examination of the values of $|F_o|$ and $|F_c|$ for strong low-order reflections suggested that the data were subject to secondary extinction. A correction of the type described by Zachariasen was applied[16,17] giving a value of 1.0 (2) × 10^{-8} for the extinction coefficient. The value of R_2 showed no dependence on sin θ or $|F_o|$, which indicates that our weighting scheme of $p = 0.04$ is essentially correct.

In the final cycle of refinement there were 98 varied parameters including the scale factor and 803 reflections, which gives a reflection to parameter ratio of approximately 8:1. A reflection was considered observed if it had a value greater than $3\sigma(F_o^2)$, and only observed reflections were used in the least-squares refinement. In the last least-squares cycle only one parameter shifted by more than 0.4 esd, indicating that refinement had converged. The final model gave values of R_1 and R_2 of 0.032 and 0.043, respectively, and an error in an observation of unit weight of 1.87.

Examination of the final difference Fourier map revealed no peak above 0.6 e Å^{-3} except for 3.2 e Å^{-3} residual density around the platinum atom. This density around the heavy atom is presumably due to some small error in our absorption correction, which is not unexpected in view of the large value of μ_a for platinum for this radiation.

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.[18]

Description of the Structure

Molecules of $Pt(C_7H_7N_2O)_2$ stack on top of one another to form linear chains along the crystallographic c axis. The platinum atoms in the chain, which lie on centers of symmetry, are separated by 3.363 (1) Å. Thus, the Pt–Pt separation found here is intermediate between the value of approximately 3.25 Å found for the parent complex,[6] for $[Pt(NH_3)_4][PtCl_4]$ (Magnus green salt, MGS)[19] and for $[Pt(CH_3NH_2)_4][PtCl_4]$ (Me-MGS),[20] and the value of approximately 3.40 Å found for $[Pt(en)_2Cl_2]$[21] and $[Pt(C_2H_5NH_2)_4][PtCl_4]$ (Et-MGS);[20] all of these complexes show evidence of Pt–Pt interactions.[1] The molecular planes, although parallel to each other, are not parallel to the ab plane but make angles of 7.3, 88.2, and 82.9° with the ab, ac, and bc planes, respectively.

Table III. Selected Interatomic Distances and Angles in $[Pt(C_7H_7N_2O)_2]$

	Distances, Å		Angles, deg
Pt(1)–N(1)	2.019 (9)	N(1)–Pt(1)–N(2)	78.7 (4)
Pt(1)–N(2)	2.030 (9)	C(1)–N(1)–Pt(1)	114.4 (7)
N(1)–C(1)	1.36 (1)	C(1)–N(1)–C(5)	119.0 (9)
C(1)–C(2)	1.37 (1)	N(1)–C(1)–C(6)	116.1 (9)
C(2)–C(3)	1.35 (1)	N(1)–C(1)–C(2)	119.6 (10)
C(3)–C(4)	1.36 (1)	C(1)–C(2)–C(3)	120.5 (11)
C(4)–C(5)	1.36 (1)	C(2)–C(3)–C(4)	119.2 (9)
C(5)–N(1)	1.31 (1)	C(3)–C(4)–C(5)	118.7 (9)
C(1)–C(6)	1.45 (1)	C(6)–C(5)–N(1)	122.9 (11)
C(6)–C(7)	1.50 (1)	C(1)–C(6)–N(2)	113.4 (9)
C(6)–N(2)	1.32 (1)	C(1)–C(6)–C(7)	125.1 (11)
N(2)–O(1)	1.29 (1)	C(6)–N(2)–O(1)	119.5 (9)
		Pt(1)–N(2)–O(1)	123.2 (7)

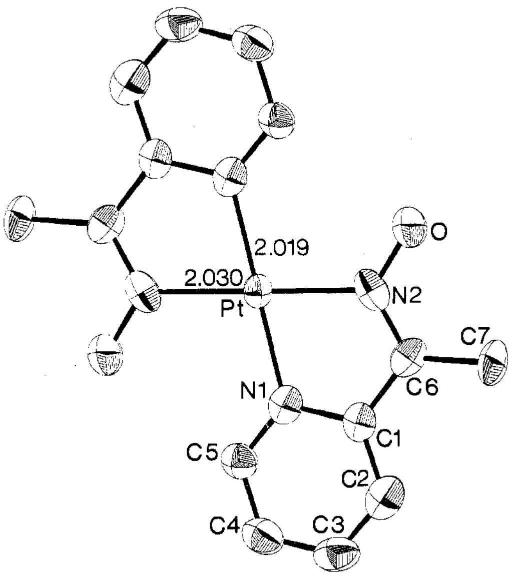

Figure 1. A single formula unit of $[Pt(C_7H_7N_2O)_2]$ viewed along the crystallographic c axis. Hydrogen atoms are omitted for clarity. The thermal ellipsoids are drawn at the 50% probability level.

A view of the molecule is presented in Figure 1. The platinum–nitrogen distances of 2.030 (9) and 2.019 (9) Å are similar to the distances found[6] for the parent molecule in this series and are also in good agreement with Pt–N distances found by other workers.[19,22] Angles in the coordination sphere of the platinum atom are 78.7 (4)° for the N(1)–Pt–N(2) angle and, of course, its supplement for the N(1)–Pt–N(2)′ angle. The distances and angles found for the pyridine rings are similar to these found previously for the parent molecule and are comparable to distances and angles found for other coordinated, substituted pyridine rings.[23-25] The C(6)–C(7) bond distance of 1.50 (1) Å agrees well with accepted values for a carbon–carbon single bond.[26] The entire complex is approximately planar, with no nonhydrogen atom deviating from the best least-squares plane through the molecule by more than 0.03 Å.

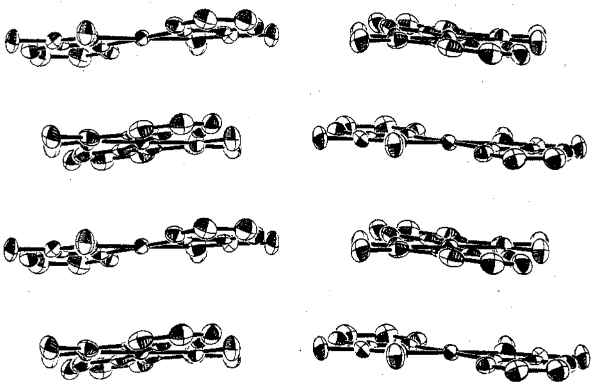

Figure 2. The stacking arrangement in the crystals of [$Pt(C_7H_7N_2O)_2$] as viewed normal to the crystallographic *c* axis.

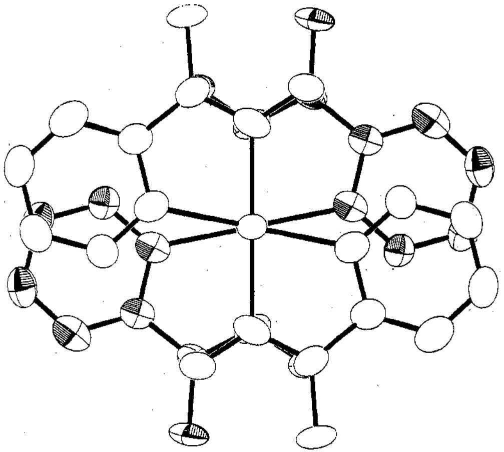

Figure 3. The stacking arrangement showing the nature of the ligand–ligand overlap as viewed parallel to the crystallographic *c* axis in the crystals of [$Pt(C_7H_7N_2O)_2$]. The shaded ellipsoids are *c*/2 (3.36 Å) below the nonshaded atoms.

The overall packing in the crystal is shown in Figures 2 and 3. In Figure 2 the view is perpendicular to the crystallographic *c* axis and shows the inter-layer separation of the molecules, as well as the amount of deviation of the molecular plane from the normal to the *c* axis. The molecules all tip in the same direction so that the inter-layer separation (which is *c*/2 or 3.363 Å) is constant for the entire molecule. A view parallel to the *c* axis is shown in Figure 3. The molecules with coordinates of $z = 0$ are shown as unshaded ellipsoids and the molecules at $z = 1/2$ are shown as shaded ellipsoids. In this view one can see that the pyridine ring moiety of the ligand has very little atom–atom overlap, but the C–N–O chain substituent is stacked virtually atom for atom on itself. In contrast, the stacking in the parent molecule[6] showed only one atom, (C(5)), stacked on top of another, C(5′); the chain part of the ligand was displaced so that the atoms were not directly over one another.

The electrical conductivity as measured from pressed pellets shows an average value of $3 \times 10^{-9}\ \Omega^{-1}\ \mathrm{cm}^{-1}$.[27] This is comparable to the value of $2 \times 10^{-9}\ \Omega^{-1}\ \mathrm{cm}^{-1}$ for the parent compound reported earlier and also similar to that found for the one-dimensional stacked iridium compound [$Ir(CO)_2acac$].[28] The [$Ir(CO)_2acac$] compound has a metal–metal distance of 3.20 Å.[29] The values for pressed pellets of Magnus green salt are $2 \times 10^{-8}\ \Omega^{-1}\ \mathrm{cm}^{-1}$ and $2.1 \times 10^{-9}\ \Omega^{-1}\ \mathrm{cm}^{-1}$,[30,31] which are also similar to the conductivity values we found. In related Pt and Ni complexes the anisotropic conductivity along the metal–metal direction of a single crystal has been shown to exceed that of the pellet sample by a factor of 10^4 or 10^5; hence these conductivity values must be regarded as lower limits.[30] We have unfortunately not yet succeeded in growing single crystals of this complex suitable for such anisotropic measurements.

This structural analysis shows a larger interplanar stacking distance, 3.363 Å, for $Pt(C_7H_7N_2O)_2$ than was found (3.245 Å) for the parent molecule. Among the reasons for this increase in distance is the larger degree of ligand–ligand overlap found in this structure. This line of reasoning would be contrary to any suggestion that the enhanced conductivity was due to π–π interactions between the ligands. Another obvious difference in the two structures is the absence of a hydrated water molecule in the present structure. This could also be partly responsible for the increased stacking distance, as the ligand, formally $(C_7H_7N_2O)^-$, has a large amount of the charge localized on the oxygen atom. The strong hydrogen bond in the parent molecule would have been a good means through which to delocalize this charge, and minimize the interaction between the oxygen atom and atoms above and below it in the stacking arrangement. The shift of the ligand plane away from the normal to the Pt–Pt or crystallographic *c* axis is somewhat unexpected from both steric and metal–metal orbital overlap points of view. There are no intra-chain atom–atom contacts shorter than that of the layer separation which might account for the tip in the molecular plane. Moreover, this tip in the molecular plane causes the d_{z^2} orbitals on the platinum atoms to no longer be strictly linearly lined up with each other. We expect the reduced metal–metal orbital overlap, both from increased layer separation and from the noncolinear d_{z^2} orbitals, to be reflected in a loss of conductivity compared to the parent compound when we are able to obtain single-crystal conductivity measurements.

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Registry No. [$Pt(C_7H_7N_2O)_2$], 59492-74-9.

Supplementary Material Available: A listing of structure factor amplitudes for $Pt(C_7H_7N_2O)_2$ (5 pages). Ordering information is given on any current masthead page.

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Contribution from the Department of Chemistry,
The University of North Carolina, Chapel Hill, North Carolina 27514

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

DANIEL W. PHELPS, W. HUGH GOODMAN, and DEREK J. HODGSON*

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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 (×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