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Metal Complexes as Ligands. VII. Copper Bromide Complexes with Bidentate Schiff Bases

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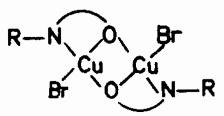
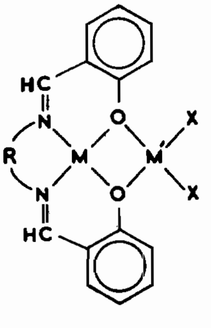
A series of new binuclear copper(II) complexes has been prepared by the reaction of copper(II) bromide with bis(N-R-salicylaldimino)copper(II) complexes, where R is a normal or branched alkyl, or a phenyl group. The room temperature magnetic moments are considerably below the « spin-only » values, due to antiferromagnetic exchange interactions between adjacent copper atoms. The ligand field absorption spectra are in keeping with only one type of copper atom, indicating that the environment about each of the two copper atoms is the same. These properties are explained in terms of a trans *structure*



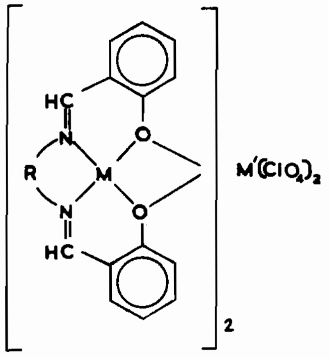
for these binuclear complexes derived from bidentate salicylaldimines, as opposed to the cis *structure for the analogous derivatives of tetradentate salicylaldimines. This* trans *structure is analogous to that proposed earlier for copper chloride complexes with bidentate Schiff Bases. The magnetic moments and the ligand field absorption spectra are not very sensitive to the size of the R- group on the nitrogen, indicating that the steric effect of these groups is fairly small, as expected for the proposed structure. The copper bromide complexes are less stable, and lower melting, than the chloride complexes. The ligand field absorption bands are at lower energies in the bromide than in the chloride complexes; this is interpreted in terms of a difference in ligand field strength as well in stereochemistry.*

Introduction

We have described the synthesis of binuclear and trinuclear complexes of the types [i],[2] [ii][1,3] and [iii][4] from metal salicylaldimine complexes, where X = Cl, Br and M and M′ may be a variety of similar or dissimilar transition or non-transition metals.



[i]



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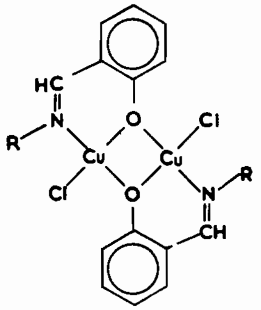

[iii]

The formation of these complexes is based on the well-known ability of the phenolic oxygen atom in salicylaldimine complexes to change its coordination number from two to three in solution,[5] thereby forming oxygen-bridges between pairs of metal atoms, and on the fact that such oxygen-bridged compounds often remain stable in the solid state.[6] The various complexes of types [i], [ii] and [iii] were characterised with the aid of magnetic susceptibility data together with electronic and infrared spectra, and synthetic and conductimetric studies.[1-4,7] In most of the bi- and tri-nuclear complexes containing paramagnetic metals held adjacent to one another by oxygen-bridges,

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(1) Part VI: S. J. Gruber, C. M. Harris and E. Sinn, *J. Chem. Phys.*, *49*, 2183 (1968).

(2) S. J. Gruber, C. M. Harris and E. Sinn, *Inorg. Chem.*, *7*, 268 (1968).

(3) S. J. Gruber, C. M. Harris and E. Sinn, *J. Inorg. Nucl. Chem.*, *30*, 1805 (1968).

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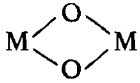
the proximity of the metals was found to result in magnetic exchange interactions.[1-4,7,8] In all binuclear and trinuclear complexes so far isolated, the infrared absorption observed near 1,540 cm^{-1} in the parent metal salicylaldimine complexes was found to be shifted to higher frequency by about 20 cm^{-1} as a result of the  $M\langle{}^{O}_{O}\rangle M$ bridging.[3,4,8] Similar shifts were observed in other infrared bands. The consistency of the infrared shift resulting from the oxygen-bridging is therefore a good criterion for the multinuclear complex formation.

Experimental Section

The reaction[9,10] of the copper(II) complex of salicylaldehyde with the appropriate primary amines was used to obtain the bis(N-substituted salicylaldimino)-copper(II) complex used as starting materials (« ligands ») in the preparations of the binuclear complexes. These starting materials were characterised by their melting points, magnetic moments and electronic spectra, all of which were found to be in good agreement with the literature values,[4,9,10,11] and are further discussed below.

Bromo(N-methylsalicylaldimino)copper(II). Bis(N-methylsalicylaldimino)copper(II) (6.5 g) was dissolved in a minimum volume of a boiling mixture of chloroform (50%) and methanol (50%) and the solution treated with a concentrated solution of copper(II) bromide (5.0 g) in hot ethanol. The mixture was covered and allowed to stand overnight, and the dark green crystalline product was then filtered off. *Anal. Calcd.* for $C_{16}H_{16}N_2O_2Br_2Cu_2$; C, 34.6; H, 2.9; N, 5.0; Br, 28.8; Cu, 22.9. Found: C,34.3; H, 3.1; N, 4.7; Br, 28.6; Cu, 23.2.

Bromo(N-ethylsalicylaldimino)copper(II). Bis(N-ethylsalicylaldimino)copper(II) (7.0 g) was treated as above, and yielded lustrous black crystals. *Anal.* Calcd. for $C_{18}H_{20}N_2O_2Br_2Cu_2$: C,37.1; H,3.5; Cu, 21.8 Found: C, 36.9; H, 3.5; Cu, 21.8.

Bromo(N-n-butylsalicyladmino)copper(II). Bis(N-*n*-butylsalicylaldimino)copper(II) (8.0 g) was treated as above to form a dark green microcrystalline complex. *Anal.* Calcd. for $C_{22}H_{28}N_2O_2Br_2Cu_2$: C, 41.3; H, 4.4. Found: C, 41.4; H, 4.3.

Bromo(N-sec-butylsalicylaldimino)copper(II). Bis-(N-*sec*- butylsalicylaldimino)copper(II) (8.0 g) was boiled in ethanol (200 ml) and small portions of chloroform were added to aid solution until the complex had entirely dissolevd. A concentrated solution of copper(II) bromide (5.0 g) in hot ethanol was then added, and the mixture allowed to stand for three days. The black crystalline product was filtered off. *Anal.* Calcd. for $C_{22}H_{28}N_2O_2Br_2Cu_2$: C, 41.3; H, 4.4; N, 4.4; Cu, 19.9. Found: C, 41.1; H, 4.6; N, 4.0; Cu, 19.9.

Bromo(N-n-octylsalicylaldimino)copper(II). Bis(N-*n*-octylsalicylaldimino)copper(II) was treated as above to form a black crystalline product. *Anal.* Calcd. for $C_{30}H_{44}N_2O_2Br_2Cu_2$: C, 47.9; H, 5.9; N, 3.7; Cu, 16.9. Found: C, 48.1; H, 5.6; N, 3.2; Cu, 16.8.

Bromo(N-cyclohexylsalicylaldimino)copper(II). Bis-(N-*cyclo*hexylsalicylaldimino)copper(II) (9.0 g) was dissolved in a minimum of dichloromethane/methanol (1:1), and treated with a concentrated solution of copper(II) bromide (5.0 g) in hot ethanol. After standing for three days, the brown product was filtered off. *Anal.* Calcd. for $C_{26}H_{32}N_2O_2Br_2Cu_2$: C, 45.2; H, 4.7; Cu, 18.4. Found: C, 45.8; H, 4.7; Cu, 18.2.

Bromo(N-phenylsalicylaldimino)copper(II). Bis(N-phenylsalicylaldimino)copper(II) (9.0 g) was boiled in methanol (300 ml) and chloroform was added slowly until the complex dissolved. The solution was treated with copper(II) bromide (5.0 g) dissolved in ethanol. The mixture was allowed to stand for two days, and the black microcrystalline product was then filtered off. Anal. Calcd. for $C_{26}H_{20}N_2O_2Br_2Cu_2$: C, 46.0; H, 3.0; Cu, 18.7; Found.: C, 45.7; H, 2.7; Cu, 18.8.

The measurements of the physical quantities, below, were made by the same methods as reported previously.[2,3,12]

Results and Discussion

Formation and Appearance of the Complexes. The chloro(N-R-salicylaldimino)copper(II) complexes[4] have been found to form very readily when the parent bis(N-R-salicylaldimino)copper(II) complex is mixed with copper(II) chloride dihydrate in the presence of a suitable solvent or in the melt. These complexes are fairly stable to heat, and are not affected by boiling down to a small volume the solution formed from the mixture of solutions containing the two starting materialms. The bromo(N-R-salicylaldimino)copper(II) complexes, on the other hand, are somewhat less stable, and some of them are decomposed by melting (Table I). Although the individual solutions containing the starting materials may be heated to boiling, prolonged heating of the black solution formed when the two are mixed frequently causes reduction of the black complexes to a white, diamagnetic material containing copper(I), which was not further examined. The ready formation of the solid bromo complexes in a fairly pure state from the solutions is probably largely due to the fact that these complexes are considerably less soluble in the solvent mixtures than either the parent copper salicylaldimines or the copper bromide.

The complexes generally form as black crystalline solids, which crush to greenish brown solids. They are slowly decomposed by water. Their melting

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(10) L. Sacconi and M. Ciampolini, *J. Chem. Soc.*, 276 (1964).

(11) L. Sacconi, M. Ciampolini, and U. Campigli, *Inorg. Chem.*, *4*, 407 (1965).

(12) C. M. Harris, H. R. H. Patil, and E. Sinn, *Inorg. Chem.*, *6*, 1102 (1967).

Table I. Melting points (°C) uncorrected) of bis(N-R-salicylaldimino)-copper(II) complexes (A) and of their binuclear copper bromide (B) and copper chloride[4] (C) derivatives.

Nitrogen substituent R	A	B	C
methyl	155	180 [a]	201
ethyl	145	169	195
n-butyl	81	150	178
n-octyl	63	121	146
sec-butyl	75	158	199
*cyclo*hexyl	177	200 [a]	207
phenyl	231	(a)	189

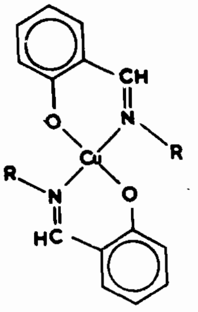
[a] decomposes.

Table II. Magnetic moments (B.M.) of bis(N-R-salicylaldimino)copper(II) complexes (A) and of their binuclear copper bromide derivatives (B).

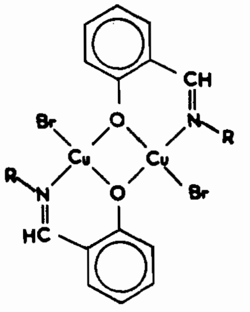
Nitrogen substituent R	A [a]	B [b]
methyl	1.81 (+3)	1.31
ethyl	1.86 (+1)	1.28
n-octyl	1.79 (−5)	1.29
sec-butyl	1.91 (−1)	1.33
*cyclo*hexyl	1.90 (−1)	1.25
phenyl	1.89 (−1)	0.86

[a] Corrected for the Weiss constants Θ (in parenthesis) using equation (1). [b] uncorrected.

points, and those of analogous chloro complexes (Table I), fall within a fairly small range, but show the expected trend with variation of the substituent R on the nitrogen atom. The parent salicylaldimine complexes have melting points (Table I) which show a similar trend, but cover a much larger range, and this is as expected since the influence of the R-group is expected to be greater in the small momonuclear salicylaldimine molecules [iv] than in the larger binuclear molecules of type [iii] or [v]. The melting points of the bromo complexes [v] are significantly lower than those of the corresponding chloro complexes [iii], but not as low as those of the parent salicylaldimines [iv].



[iv]



[v]

Magnetic Properties. The magnetic moments of the bis(N-R-salicylaldimino)-copper(II) complexes [iv] and the corresponding bromo(N-R-salicylaldimino)copper(II) complexes [v] are listed in Table II. For the parent salicylaldimines, which obey the Curie-Weiss law when measured over a temperature range,[4] the mean values of the magnetic moments corrected for the Weiss constants (Θ), were obtained from the relation

$$\mu_{corr} = \frac{1}{n} \sum_{i=1}^{n} \{8\chi_M(i)[T(i)+\Theta]\}^{1/2} \qquad (1)$$

where n is the number of determination of magnetic susceptibility $\chi_M(i)$ made at temperatures T(i). This relates to a Curie-Weiss law of the form $\chi_M \propto (T+\Theta)^{-1}$. The calculations were made with a least-squares fitting program, using an IBM 7040 computor. The moments listed for these complexes are in good agreement with the observation[4,11,12] that the magnetic moments increase as the environment about the central copper atom is increasingly distorted from planar towards tetrahedral, *i.e.* from N-methyl[13] to longer chain N-*n*-alkyl[14] to N-sec-alkyl[15] substituted complexes. For the other complex, bis(N-phenylsalicylaldimino)-copper(II), the moment lies between the values for the N-n-alkyl and N-sec-alkyl compounds; however, single crystal X-ray studies have shown the N-phenyl compound to be fairly close to planar.[16]

The magnetic moments of the binuclear bromo complexes are generally very close to 1.3 B.M., and no appreciable dependence upon the bulkiness of the substituent R on the nitrogen is observed. Thus the small individual differences are probably due to lattice effects as much as internal steric interference involving the R-groups. The phenyl complex alone is exceptional, with a significantly lower moment, which is most likely also due to lattice effects. This independence of the size of the R-group is quite in keeping with the *trans* structure [v] in which the steric interactions with the R-groups, and the resulting distortion of the environment about the copper atoms, are minimal. A *cis* structure similar to [i] would involve the R-groups in marked steric interactions with each other, and hence a dramatic dependence of the environment about the copper atoms and of the properties of the complex, upon the size of R. The phenyl complex is definitely exceptional, with a magnetic moment value of only 0.86 B.M. This might be due to strong interactions between adjacent pairs of molecules of type [v] as well as within the molecules.

The magnetic moments per copper atom for these binuclear complexes are all considerably below the «spin-only» value of 1.73 B.M. for copper(II). Such lowering of the magnetic moments has been observed in all the bi- and tri-nuclear complexes of types [i], [ii] and [iii] which contained only copper(II), and has been shown to arise from antiferromagnetic exchange interactions in each case.[1-4,7] The observed magnetic moments indicate a fairly strong exchange interaction between pairs of neighbouring copper atoms in the bromo complexes, a phenomenon which occurs in a large number of copper(II) complexes.[17]

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(14) E. N. Baker, G. R. Clark, D. Hall, and T. N. Waters, *J. Chem. Soc.* (A), 252 (1967); T. P. Cheeseman, D. Hall and T. N. Waters, *J. Chem. Soc.* (A), 694 (1966); L. Sacconi and I. Bertini, *Inorg. Chem.*, 5, 1520 (1966).

(15) P. L. Orioli and L. Sacconi, *J. Am. Chem. Soc.*, 88, 277 (1966); T. P. Cheeseman, D. Hall, and T. N. Waters, *J. Chem. Soc.* (A), 685 (1966).

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(17) M. Kato, H. B. Jonassen, and J. C. Fanning, Chem. Rev., 99 (1964).

Table III. Ligand field absorption spectra (cm^{1-}) of bis(N-R-salicylaldimino)copper(II) complexes (A) and of their copper bromide (B) and copper chloride[4] derivatives (C), in Nujol mulls.

Substituent R	A		B			C	
methyl	16900	15100	(20800)	13200	—	14800	12200
ethyl	16400	15100	(21000, sh)	—	11200	16100	12600
n-butyl	16500	—	(20400, sh)	12800	9800 (sh)		
n-octyl	16200	13200	(21000, sh)	—	10800		
sec-butyl	13300	8600	(21000, sh)	11500 (sh)		14000	10900
*cyclo*hexyl	13400	8500	(21500, sh)	12800	8500 (sh)	14100	11000
i-propyl	14000	9000				14200	11300
t-butyl	13100	8500				13100	10700
phenyl			(21000, sh)	12800	9800		

sh = shoulder Bands in parenthesis under (B) indicate a high intensity visible absorption which partially obscures the ligand field region.

Table IV. Infrared absorption peaks (cm^{-1}) in the region 700-3000 cm^{-1} for the complex bis(N-methylsalicylaldimino)copper(II) (A) and its copper bromide (B) and copper chloride (C) derivatives. Approximate intensities are given as s = strong, m = medium, w = weak and vw = very weak.

A	B	C	Assignment
1632 s	1638 s	1639 s	C=N stretch
1598 m	1598 m	1598 m	C=C aromatic
1543 m	1563 m, 1550 w	1562 m	C—O stretch
1472 s	1476 s	1479 s	C=C aromatic
1455 s	1448 s	1451 s	C—H deformation
1411 w	1410 vw	1413 w	=CH in-plane deformation
1395, 1378 w	1380 m	1382 w	C—N
1352, 1332 s		1350, 1320 w	
	1276 s	1275 s	
	1250 m	1249 m	
	1210 m	1210 m	
1194 m			
	1154 m	1153 m	
1139 w	1142 w	1143 m	Aromatic in-plane deformation region
1112 w	1125, 1115 w	1116 w	
	1187 vw		
1035 w	1040 w	1016 m	
	1018 m		
980 w	982 w	981 w	
970 w			
931 w		942 vw	CH_3 - skeletal vibrations
911 m	907 m	907 m	
849 m	853 w	856 w	=CH wag
	812 w		
805 m	803 m	798 m	
752 s	768 w	766 s	C—H wag
732 m	730 vw		

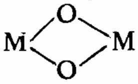
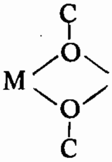
Electronic Spectra. It has been shown[10] that, in accordance with theoretical considerations, ligand field absorptions in the region 18,000-8,000 cm^{-1} in copper complexes with bidentate salicylaldimines [iv] move to lower energies as the environment about the copper atom tends from planar to tetrahedral. Similar conclusions have been drawn about the copper(II) complexes with tetradentate salicylaldimines[2,7] and with 2,2′-biquinolyl.[12] The parent copper(II) salicylaldimines [iv] have two ligand field bands in the region 18,000-8000 cm^{-1} and these show the expected trend. In the binuclear bromo complexes [v] the same two bands (Table III) suggest a similar trend, but it is very slight, and this again indicates that the copper environment is little affected by the size of the substituent R on the nitrogen, as would be expected from the structure [v]. In some cases, it was not possible to observe both of the bands in the region 18,000 - 8000 cm^{-1} because of the interference of the intense charge transfer bands in the near u.v.-vis. region. However, it is obvious that no new bands appear when the mononuclear parent complexes are converted into the binuclear bromo complexes. This suggests that the environment about each copper atom is the same, as in structure [v].

The above conclusions may also be drawn about the chloro complexes [iii] in going down the column C in Table III. There are also interesting spectral shifts observed in going across the table from a particular parent salicylaldimine complex to the appropriate bromo and chloro derivatives. For example, the ligand field absorption bands occur at significantly lower energies in the bromo than in the chloro complexes. However, these shifts cannot be explained in terms of changes in the stereochemistry about the series. The shifts observed across the table must therefore be attributed to the combined effects of the changes in ligand field energies and stereochemistries. The bromo and chloro complexes should have fairly similar stereochemistries, and the ligand field difference is probably the largest effect.

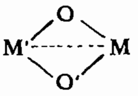
Infrared Spectra. Table IV gives the infrared absorptions observed in bis(N-methylsalicylaldimino)copper(II) and its binuclear derivatives, together with a list of assignments from the recent literature,[3,4,18-20] which appear compatible with the present observations. The band near 1540 cm^{-1} had originally been assigned to the C=N stretching vibration,[18] but the large shift in this band when oxygen-bridged complexes are formed, suggests that it is associated with the phenolic C-O bond. A similar effect is observed in analogous bands between 1500 and 1600 cm^{-1} in bis(acetylacetonato)copper(II) and N,N'-ethylenebis-(acetylacetoneimino)copper(II) when these are reacted like the salicylaldimine complexes to form multinuclear compounds.[21] In bis(acetylacetonato)copper(II), the C-O stretching modes are known to occur in this region.[22] Moreover, infrared data on salicylaldimine complexes containing N^{15} has confirmed that the C=N vibration does not absorb near 1540 cm^{-1}.[19]

Table V. Position of the infrared peak near 1540 cm^{-1} in bis(N-R-salicylaldimino)copper(II) complexes (A) and their copper bromide derivatives (B).

Substituent R	A	B
methyl	1543 m	1563 m, 1550 w
ethyl	1541 m	1563 m
n-buthyl	1542 m	1560 m
n-octyl	1540 m	1652 m
*cyclo*hexyl	1543 m	1558 m, 1555 w
sec-butyl	1541 m	1563 m
phenyl	1544 m	1557 m, 1548 m

Table V compares the position of this band in a series of mononuclear salicylaldimine [iv] and oxygen-bridged bromo [v] complexes. The increasing constraint imposed upon the vibrations in going from the parent [iv] to the binuclear complexes [iii], [v], as well as in the formation of other multinuclear complexes, is shown by significant shifts to higher energies, in bands near 1620, 1480, 1140 and 760 cm^{-1}. New bands appear near 1275, 1210 and 1150 cm^{-1}, the bands near 1190 and 970 cm^{-1} vanish, and the band near 910 cm^{-1} is lowered in energy. Comparisons between the parent salicylaldimines and their copper chloride adducts[4] cannot resolve definitely whether these differences between their infrared spectra are due entirely to the formation of  bridges, or the presence of the halogen atom. However when these spectra are compared with those of the copper bromide adducts in Table IV, it becomes obvious that the changes in the infrared spectra are not significantly dependent on the type of halogen atom in the binuclear complex, and can therefore only the be associated with the binuclear complex formation. Some of the new bands most likely arise from some kind of vibrational modes of the  skeleton, but more specific assignments do not seem profitable at this stage, and confirmation with the aid of O^{18}-bridged complexes would be desirable.

Structures of the Complexes. In addition to the experimental evidence for the *trans* structure [iii] or [v] for the binuclear complexes, this structures seems more likely *a priori*, firstly because the steric interference of the R-groups in the corresponding *cis* structure, analogous to [i], would require extreme distortion from planar toward tetrahedral stereochemistry, which is disfavoured in copper(II) complexes, and secondly for entropy reasons. The same reasoning would predict a *trans* structure for the parent salicylaldimine complexes [iv] rather than the corresponding *cis* structure, and X-ray work has confirmed this.[14] A tetrahedral stereochemistry is even further disfavoured in the binuclear complexes because of the close approach of the two copper atoms that would be required by proper tetrahedra. The metal-metal distance MM' in an arrangement of this type [vi] is given by equation (2).

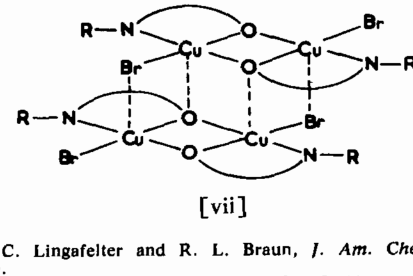


[vi]

$$MM' = 2.MO.\cos\left(\frac{OMO'}{2}\right) \qquad (2)$$

If M and M' are planar copper atoms OMO' = 90°, and MM' = MO$\sqrt{2}$. If M and M' are tetrahedral, OMO' = 109°28' and MM' = 1.155 MO. Thus, assuming a (large) value of 1.9 Å for MO,[23] MM' = = 2.7 Å for square planar metal atoms, and MM' = = 2.2 Å for tetrahedra.

The solubility and low melting points of the bromo complexes rule out strong intermolecular bonding to form a more polymeric structure than [v]. However, experience with other copper complexes[24,25] suggests that the packing of the binuclear molecules in the solid is likely to be such that weak Cu—O and Cu—Br links might exist between pairs of molecules, [vii],



[vii]

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even though these links would undoubtedly be much too weak to be formally called bonds. Electrostatic repulsion between the O and Br ligands is likely to cause sufficient distortion from planar towards tetrahedral stereochemistry to prevent more than two molecules from being linked in this way. Whether the pair of oxygens indicated in [vii], or the other pair, are involved in the linking will depend on the extent of distortion from planar to tetrahedral stereochemistry.

Only three-dimensional X-ray studies will provide the complete structures, but clearly, considerable information is available from the results of other physical measurements.