

# Stereochemical Activity of Lone Pairs. The Crystal and Molecular Structure of a Complex of 18-Crown-6(1,4,7,10,13,16-Hexaoxacyclooctadecane) with Bismuth(III) Chloride

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## Abstract

The crystal structure of a complex formed between  $\text{BiCl}_3$  and 18-crown-6(1,4,7,10,13,16-hexaoxacyclooctadecane, L) has been determined from X-ray diffractometer data by Patterson and Fourier methods. Crystals are monoclinic, space group  $Pa$ , with  $Z = 2$  in a unit cell of dimensions  $a = 15.09(1)$ ,  $b = 16.60(1)$ ,  $c = 7.987(8)$  Å,  $\beta = 103.0(1)^\circ$ . The structure, which refined to  $R = 0.058$  for 2766 observed reflections, consists of discrete  $\text{BiCl}_3 \cdot \text{H}_2\text{O} \cdot \text{L}$  (1) and  $\text{BiCl}_3 \cdot \text{L}$  (2) molecules. In 2 bismuth is sandwiched between two essentially parallel planes containing six oxygens and three chlorines, respectively, and in 1 between three ether and a water oxygen and three chlorines, respectively. In 1 there is intramolecular hydrogen bonding between the water molecule and two of the two ether oxygen atoms not bonded to the metal.

## Introduction

Complexes formed from macrocyclic polyethers (crown ethers) and p-block elements have been little studied relative to those containing other elements or organic acceptor molecules.  $^{119}\text{Sn}$  Mössbauer spectroscopy [1] and X-ray diffraction [2–4] studies on some tin(II) and tin(IV) complexes with 15-crown-5 (15CR5) (i.e. 1,4,7,10,13-pentaoxacyclopentadecane) and 18-crown-6 (18CR6) (or 1,4,7,10,13,16-hexaoxacyclooctadecane) and an X-ray study [5] on an antimony(III) complex with 15-crown-5 ( $\text{SbCl}_3 \cdot 15\text{CR5}$ ) have been reported. The work on the 15-crown-5 and 18-crown-6 tin(II) complexes – ( $15\text{CR5}$ ) $_2\text{Sn}^{2+}(\text{SnCl}_3^-)_2$  and  $\text{Sn}(18\text{CR6})\text{Cl}^+\text{SnCl}_3^-$  – show that they differ considerably from adducts containing smaller cyclic ethers, such as 1,4-dioxane [6, 7], in that the tin atoms are incorporated into molecular cations. Moreover, the ( $15\text{CR5}$ ) $_2\text{Sn}^{2+}$ -

( $\text{SnCl}_3^-$ ) $_2$  complex stands out because the tin lone pair is not sterically active [4]. To a significant extent a similar effect is observed in the  $\text{Sn}(18\text{CR6})\text{Cl}^+\text{SnCl}_3^-$  complex in which the tin atom in the complex cation exhibits much reduced stereochemical activity [3].

Although ideal  $\text{Sn}^{2+}$  and  $\text{Sb}^{3+}$  cations are iso-electronic, the fact that the ionisation energy for the latter is more than twice that of the former (2119.8 and 4872.0  $\text{kJ mol}^{-1}$ ) [8] must be a major factor governing the choice of the neutral discrete  $\text{SbCl}_3 \cdot 15\text{CR5}$  adduct rather than an ionic alternative which would have been analogous to the tin(II) systems. On going to antimony's heavier congener, bismuth, we note that the corresponding ionisation energy is very similar (4779.0  $\text{kJ mol}^{-1}$ ), which again should contribute significantly in precluding complex ionic species. Consistent with this, we find [9] that the bismuth(III) chloride adduct  $\text{BiCl}_3 \cdot 15\text{CR5}$  is iso-structural with the antimony complex.

We report here the results of a crystal structure determination on the putative  $\text{BiCl}_3 \cdot 18\text{CR6}$  adduct.

## Experimental

### Preparation

Crystals of the complex were obtained by mixing solutions of  $\text{BiCl}_3$  (0.16 g) and 18-crown-6 (0.12 g) in acetone (total volume 5  $\text{cm}^3$ ) and allowing the solvent to evaporate slowly for several days.

### Crystallography

#### Crystal data

$\text{C}_{24}\text{H}_{50}\text{Cl}_6\text{O}_{13}\text{Bi}_2$ ,  $M = 1177.3$ , monoclinic,  $a = 15.09(1)$ ,  $b = 16.60(1)$ ,  $c = 7.987(8)$  Å,  $\beta = 103.0(1)^\circ$ ,  $U = 1949.42$  Å $^3$ ,  $D_c = 2.00$   $\text{g cm}^{-3}$ ,  $D_m = 1.94$   $\text{g cm}^{-3}$ ,  $F(000) = 1132$ ,  $Z = 2$ , Mo  $K\alpha$  radiation,  $\lambda = 0.71069$  Å,  $\mu = 90.7$   $\text{cm}^{-1}$ , space group  $Pa$ .

### Intensity Data Collection and Structure Refinement

A crystal of approximate size  $0.3 \times 0.3 \times 0.3$  mm was mounted so as to rotate about the  $a$  axis on a Stoe STADI2 diffractometer and data were collected via a variable-width  $\omega$  scan. Background counts were for 20 s and a scan rate of  $0.0333^\circ \text{ s}^{-1}$  was applied to a width of  $(1.5 + \sin\mu/\tan\theta)$ . The intensities of 3405 independent reflections were measured out to  $2\theta < 50^\circ$  using monochromatised Mo  $K\alpha$  radiation. Of these, 2766 reflections were classified as observed, i.e.  $I_{\text{net}} > 3.0\sigma(I)$ , and used in the refinement. Lorentz and polarisation corrections were applied, systematic absences rejected and equivalent reflections merged. The crystal was stable under data collection. Scattering factors and dispersion corrections were taken from ref. 10; bismuth values being used for bismuth(III). The structure was solved by Patterson and Fourier methods. Calculations were carried out on an Amdahl V7 computer using the SHELX 76 package [11] and its full matrix least-squares methods with the weighting scheme  $w = 1/[\sigma^2(F) + 0.003F^2]$  and successfully refined in space group  $P\bar{4}3m$  to a final  $R$  factor of 0.058 ( $R_w = 0.065$ ) with anisotropic thermal factors for the non-hydrogen atoms. The data were corrected empirically for absorption [12] and hydrogen atoms placed in calculated positions and given a common refined thermal parameter. Those on the water molecule were not located or positioned. The final  $R$  value was 0.058 ( $R' 0.065$ ), this solution being chosen rather than the reversed coordinate (i.e.  $-x, -y, -z$ ) solution which gave an  $R$  value of 0.062.

The atomic positions are given in Table 1, and Table 2 contains the interatomic distances and valence angles.

### Results and Discussion

The asymmetric unit consists of the two discrete neutral molecules  $\text{BiCl}_3 \cdot \text{H}_2\text{O} \cdot 18\text{CR6}$  (coordination number 7) and  $\text{BiCl}_3 \cdot 18\text{CR6}$  (coordination number 9). As shown in Figs. 1 and 2, these two different complex molecules (designated molecules 1 and 2, respectively) have common features; thus, it is possible to discern pyramidal  $\text{BiCl}_3$  units in both molecules, the Cl–Bi–Cl angles all being close to  $90^\circ$ , ranging from  $87.0(3)$  to  $92.9(3)^\circ$ . The Bi–Cl bond lengths in both units are experimentally indistinguishable, being 2.483(9), 2.495(11), 2.506(11) Å and 2.478(11), 2.500(9), 2.556(10) Å for 1 and 2, respectively. While the influence of the ligand and crystal packing forces have no significant effect on the Bi–Cl bonds the Cl–Bi–Cl angles (average differences  $12^\circ$ ) are decreased relative to the angles ( $97.3^\circ$ ) in gas-phase bismuth(III) chloride [13]. Only a few structures of complexes of bismuth(III) chloride are known; the Cambridge Data File contains

TABLE 1. Atomic coordinates ( $\times 10^4$ ) with e.s.d.s in parentheses

Atom	$x$	$y$	$z$
Bi(1)	0 <sup>a</sup>	1473(1)	0 <sup>a</sup>
Cl(1)	−1354(6)	816(6)	894(11)
Cl(2)	1129(7)	790(7)	2341(12)
Cl(3)	−100(8)	2629(6)	1912(13)
O(100)	1200(15)	2291(16)	−925(26)
O(1)	902(12)	473(15)	−2046(24)
C(2)	1770(22)	186(26)	−1522(53)
C(3)	2363(29)	566(25)	−2536(38)
O(4)	2448(16)	1361(17)	−2163(35)
C(5)	2970(34)	1829(33)	−3113(77)
C(6)	2967(30)	2645(29)	−2816(48)
O(7)	2084(23)	2922(19)	−3581(43)
C(8)	1949(35)	3761(25)	−3292(58)
C(9)	999(23)	3953(26)	−3953(59)
O(10)	459(21)	3609(15)	−2914(33)
C(11)	−542(38)	3736(22)	−3545(68)
C(12)	−992(36)	3308(22)	−2472(69)
O(13)	−963(17)	2467(15)	−2547(29)
C(14)	−1414(26)	2155(25)	−4147(45)
C(15)	−1657(29)	1310(27)	−3983(59)
O(16)	−927(15)	827(17)	−3205(31)
C(17)	−370(26)	589(25)	−4302(43)
C(18)	386(38)	129(21)	−3519(45)
Bi(2)	5474(1)	3256(1)	3687(2)
Cl(4)	6860(6)	4043(6)	4973(13)
Cl(5)	4740(7)	3910(7)	5860(12)
Cl(6)	6025(8)	2164(7)	5814(13)
O(21)	6707(18)	2474(17)	1897(32)
C(22)	7188(51)	2939(44)	935(35)
C(23)	6705(28)	3566(33)	−108(63)
O(24)	6206(25)	3993(21)	799(31)
C(25)	5928(26)	4633(27)	3(59)
C(26)	5631(29)	5156(25)	1248(64)
O(27)	5019(17)	4754(20)	1998(37)
C(28)	4118(24)	4940(30)	1109(102)
C(29)	3436(21)	4538(35)	1920(92)
O(30)	3491(15)	3779(16)	1777(33)
C(31)	2864(30)	3407(35)	2516(73)
C(32)	2931(40)	2489(28)	2333(62)
O(33)	3760(18)	2246(14)	3305(30)
C(34)	3922(57)	1490(34)	3216(70)
C(35)	4423(56)	1228(33)	1712(76)
O(36)	4996(26)	1804(21)	1535(52)
C(37)	5531(86)	1588(78)	759(146)
C(38)	6423(36)	1846(35)	905(75)

just three. In one of these the  $\text{BiCl}_3$  fragment is in a T-arrangement [14]; in the other two the fragment shows a geometry similar to the present compound [15, 16]. In addition to these, a recent structure determination [17] on  $\text{BiCl}_3 \cdot 15\text{CR5}$  also contains a pyramidal  $\text{BiCl}_3$  unit.

In part, the present 18-crown-6 structure differs from the antimony(III) chloride and bismuth(III) adducts,  $\text{SbCl}_3 \cdot 15\text{CR5}$  and  $\text{BiCl}_3 \cdot 15\text{CR5}$  (see above) because these are built up from a single type of

TABLE 2. Molecular dimensions in the coordination spheres: distances (Å), angles (°)

Molecule 1	
Bi(1)–Cl(1)	2.556(10)
Bi(1)–Cl(2)	2.500(9)
Bi(1)–Cl(3)	2.478(11)
Bi(1)–O(100)	2.504(25)
Bi(1)–O(1)	2.877(23)
Bi(1)–O(13)	2.765(23)
Bi(1)–O(16)	2.837(23)
Cl(1)–Bi(1)–Cl(2)	92.9(3)
Cl(1)–Bi(1)–Cl(3)	89.7(4)
Cl(2)–Bi(1)–Cl(3)	90.9(3)
Cl(1)–Bi(1)–O(100)	172.1(6)
Cl(2)–Bi(1)–O(100)	92.9(5)
Cl(3)–Bi(1)–O(100)	84.8(6)
Cl(1)–Bi(1)–O(1)	115.0(5)
Cl(2)–Bi(1)–O(1)	80.4(4)
Cl(3)–Bi(1)–O(1)	154.0(5)
O(100)–Bi(1)–O(1)	71.3(7)
Cl(1)–Bi(1)–O(13)	98.0(5)
Cl(2)–Bi(1)–O(13)	167.9(5)
Cl(3)–Bi(1)–O(13)	84.0(5)
O(100)–Bi(1)–O(13)	75.8(7)
O(1)–Bi(1)–O(13)	99.4(6)
Cl(1)–Bi(1)–O(16)	80.1(5)
Cl(2)–Bi(1)–O(16)	128.2(5)
Cl(3)–Bi(1)–O(16)	139.7(5)
O(100)–Bi(1)–O(16)	100.4(7)
O(1)–Bi(1)–O(16)	58.0(6)
O(13)–Bi(1)–O(16)	59.4(7)
Molecule 2	
Bi(2)–Cl(4)	2.483(9)
Bi(2)–Cl(5)	2.506(11)
Bi(2)–Cl(6)	2.495(11)
Bi(2)–O(21)	2.896(29)
Bi(2)–O(24)	3.031(32)
Bi(2)–O(27)	2.839(31)
Bi(2)–O(30)	3.159(21)
Bi(2)–O(33)	3.040(26)
Bi(2)–O(36)	2.954(37)
Cl(4)–Bi(2)–Cl(5)	87.0(3)
Cl(4)–Bi(2)–Cl(6)	88.9(3)
Cl(5)–Bi(2)–Cl(6)	88.5(4)
Cl(4)–Bi(2)–O(21)	82.3(5)
Cl(5)–Bi(2)–O(21)	165.7(5)
Cl(6)–Bi(2)–O(21)	81.8(6)
Cl(4)–Bi(2)–O(24)	71.7(6)
Cl(5)–Bi(2)–O(24)	130.2(7)
Cl(6)–Bi(2)–O(24)	133.5(7)
O(21)–Bi(2)–O(24)	54.6(8)
Cl(4)–Bi(2)–O(27)	80.1(5)
Cl(5)–Bi(2)–O(27)	81.5(6)
Cl(6)–Bi(2)–O(27)	165.4(6)
O(21)–Bi(2)–O(27)	105.8(8)
O(24)–Bi(2)–O(27)	51.3(9)
Cl(4)–Bi(2)–O(30)	132.3(5)

(continued)

TABLE 2. (continued)

Molecule 2	
Cl(5)–Bi(2)–O(30)	72.4(5)
Cl(6)–Bi(2)–O(30)	131.5(5)
O(21)–Bi(2)–O(30)	121.9(6)
O(24)–Bi(2)–O(30)	89.4(8)
O(27)–Bi(2)–O(30)	55.1(7)
Cl(4)–Bi(2)–O(33)	161.8(5)
Cl(5)–Bi(2)–O(33)	79.0(5)
Cl(6)–Bi(2)–O(33)	79.2(5)
O(21)–Bi(2)–O(33)	109.2(7)
O(24)–Bi(2)–O(33)	126.4(7)
O(27)–Bi(2)–O(33)	109.0(6)
O(30)–Bi(2)–O(33)	53.9(6)
Cl(4)–Bi(2)–O(36)	137.9(8)
Cl(5)–Bi(2)–O(36)	131.9(8)
Cl(6)–Bi(2)–O(36)	78.7(7)
O(21)–Bi(2)–O(36)	56.4(9)
O(24)–Bi(2)–O(36)	88.3(10)
O(27)–Bi(2)–O(36)	115.9(9)
O(30)–Bi(2)–O(36)	82.1(8)
O(33)–Bi(2)–O(36)	53.2(9)
Torsion angles	
C(18)–O(1)–C(2)–C(3)	80.3
C(2)–O(1)–C(18)–C(17)	–161.3
O(1)–C(2)–C(3)–O(4)	66.7
C(2)–C(3)–O(4)–C(5)	–176.9
C(3)–O(4)–C(5)–C(6)	174.0
O(4)–C(5)–C(6)–O(7)	–70.6
C(5)–C(6)–O(7)–C(8)	176.3
C(6)–O(7)–C(8)–C(9)	–173.3
O(7)–C(8)–C(9)–O(10)	71.0
C(8)–C(9)–O(10)–C(11)	–176.9
C(9)–O(10)–C(11)–C(12)	175.2
O(10)–C(11)–C(12)–O(13)	–68.6
C(11)–C(12)–O(13)–C(14)	–65.0
C(12)–O(13)–C(14)–C(15)	–159.0
O(13)–C(14)–C(15)–O(16)	–53.6
C(14)–C(15)–O(16)–C(17)	–79.7
C(15)–O(16)–C(17)–C(18)	177.6
O(16)–C(17)–C(18)–O(1)	–51.6
C(38)–O(21)–C(22)–C(23)	93.9
C(22)–O(21)–C(38)–C(37)	–136.3
O(21)–C(22)–C(23)–O(24)	45.8
C(22)–C(23)–O(24)–C(25)	167.1
C(23)–O(24)–C(25)–C(26)	–164.2
O(24)–C(25)–C(26)–O(27)	–53.1
C(25)–C(26)–O(27)–C(28)	–95.1
C(26)–O(27)–C(28)–C(29)	–178.1
O(27)–C(28)–C(29)–O(30)	–65.1
C(28)–C(29)–O(30)–C(31)	–179.8
C(29)–O(30)–C(31)–C(32)	179.8
O(30)–C(31)–C(32)–O(33)	66.5
C(31)–C(32)–O(33)–C(34)	–177.4
C(32)–O(33)–C(34)–C(35)	89.9
O(33)–C(34)–C(35)–O(36)	35.2
C(34)–C(35)–O(36)–C(37)	163.9
C(35)–O(36)–C(37)–C(38)	–149.6
O(36)–C(37)–C(38)–O(21)	–8.1

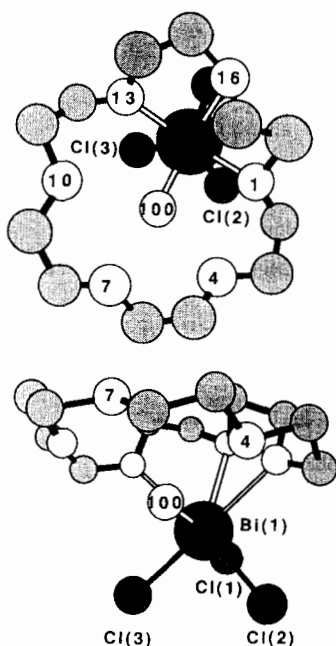


Fig. 1. The  $\text{BiCl}_3 \cdot 18\text{CR6} \cdot \text{H}_2\text{O}$  (molecule 1).

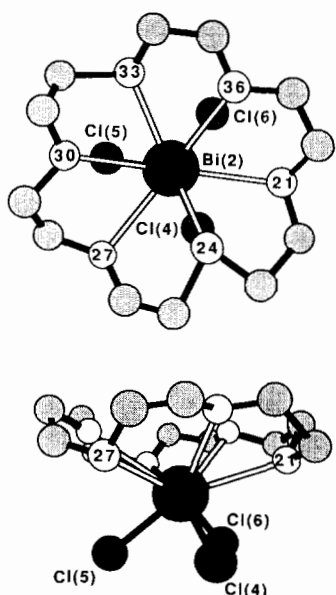


Fig. 2. The  $\text{BiCl}_3 \cdot 18\text{CR6}$  (molecule 2).

molecule, i.e. containing distinct  $\text{SbCl}_3$  or  $\text{BiCl}_3$  units complexed to *all* five oxygens of the crown ether [5, 17], although reminiscent of molecule 2 with the  $\text{BiCl}_3$  unit (here being bonded to all six oxygens of the 18-crown-6) molecule 1 is different.

Although molecule 1 is bound to an extra ligand – the water molecule – it does have the common structural feature with molecule 2 (and also  $\text{SbCl}_3 \cdot 15\text{CR5}$  and  $\text{BiCl}_3 \cdot 15\text{CR5}$ ) of the apex of the pyramidal  $\text{BiCl}_3$  units being directed towards the

cavity encircled by the 18-crown-6 ligand. However, only in molecule 2 does the  $\text{BiCl}_3$  apex point towards the centre itself of the periphery defined by the six crown oxygen atoms (which we designate  $\text{O}_6$ ), and of the two it is this molecule which bears the closest similarity to the  $\text{SbCl}_3 \cdot 15\text{CR5}$  and  $\text{BiCl}_3 \cdot 15\text{CR5}$  complexes. Molecule 1 differs in that the same apex is clearly directed off-centre with regard to the  $\text{O}_6$  grouping so that instead it is more appropriate to invoke an  $\text{O}_3$  arrangement with an additional bond to the water.

It is evident that incorporating the water ligand into the complex in this way displaces the  $\text{BiCl}_3$  unit to one end of the crown ether so that bismuth now interacts directly with only three ether oxygens instead of the full complement of six. These three non-bonded  $\text{Bi}-\text{O}$  distances are all in excess of 3.75 Å. That the water molecule is relatively strongly bound to bismuth is shown by the  $\text{Bi}-\text{O}$  distance of 2.504(25) Å. The comparatively close contacts ( $\text{O}(4)$  2.76(4),  $\text{O}(7)$  2.94(5),  $\text{O}(10)$  2.79(4) Å) between the water molecule and the  $\text{O}_3$  grouping, together with the geometry are consistent with the presence of intramolecular H bonding. Relevant angles are  $\text{Bi}-\text{O}(100)\dots\text{O}(4)$   $114^\circ$ ,  $\text{Bi}-\text{O}(100)\dots\text{O}(14)$   $112^\circ$ ,  $\text{O}(4)\dots\text{O}(100)\dots\text{O}(10)$   $117^\circ$ . There is no precedent (based on a search of the files of the Cambridge Data Centre) for a metal atom bonded to both water and to the oxygen atoms of 18-crown-6 and being simultaneously connected via hydrogen bonds between the water and the unbonded oxygens of the crown. There are no intermolecular hydrogen bonds in the structure.

It is of interest to compare the present structure with other complexes of large metal atoms with 18-crown-6. As we have already discussed [3, 18], in several structures the metal atom occupies the cavity of the crown and the macrocycle is approximately in the  $D_{3d}$  conformation. The ideal  $\text{M}-\text{O}$  distance for metal (M) complexes with the 18-crown-6 in this conformation is 2.85 Å [3]. Examples are with  $\text{K}^+$ ,  $\text{Cd}(\text{II})$ ,  $\text{Sn}(\text{II})$ ,  $\text{Hg}(\text{II})$  and  $\text{Pb}(\text{II})$  (mean  $\text{M}-\text{O}$  distances 2.80, 2.75, 2.75, 2.85 and 2.75 Å, respectively). In these examples, the metal atoms are either mono- or divalent and are solely bound to the macrocycle in a molecular cation. However, the formation of complexed  $\text{Sb}^{3+}$  or  $\text{Bi}^{3+}$  is not so readily achieved (see above) and the complexes instead are molecular adducts of  $\text{SbCl}_3$  and  $\text{BiCl}_3$ , and the conformations of the 18-crown-6 molecules are irregular; the least-squares plane for the six oxygen atoms of molecule 2 is essentially parallel (with a  $0.5^\circ$  angle of intersection) to the plane of the three chlorine atoms. Hence, we describe the bismuth atom, as is also the case for the antimony and bismuth atoms in  $\text{SbCl}_3 \cdot 15\text{CR5}$  and  $\text{BiCl}_3 \cdot 15\text{CR5}$ , respectively, as being sandwiched between a three-membered ring of chlorines on one side and the six-membered – or

five-membered in the case of the 15CR5 adducts — ring of oxygen atoms on the other. Even molecule 1 is compatible with this description in that the four oxygen atoms bonded to the metal (one water and three ether oxygens) form an approximate plane (maximum deviation 0.03 Å) and this plane is approximately parallel to that of the three chlorine atoms (angle  $9.6^\circ$ ).

The influence of the crown ethers on the bismuth lone pair is of course central to any detailed discussion on the molecule. Evidence that the lone pair retains much of its stereochemical activity — albeit somewhat modified by interaction with the  $O_6$  grouping — is lent support by the structural integrity of the  $BiCl_3$  fragment. Again, this is similar to  $SbCl_3 \cdot 15CR5$  and  $BiCl_3 \cdot 15CR5$  but departs from the structural behaviour shown by the tin(II) adducts (see above). We omit a detailed discussion on the nature of the lone pair since the background for this has been presented recently in ref. 3 (and refs. therein). Suffice it to state that the bismuth lone pair can be identified with contributions from the 6s and 6p orbitals and is explicitly represented by the sum of antibonding molecular orbitals with their varying bismuth or ligand character. The geometry adopted reflects the desire of the system to attain a lower total energy through maximum population of the bismuth lower 6s valence orbital. This end is achieved through distortions which are appropriate in the context of all the other energies that are germane to the system as a whole.

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