CIS-TRIHETERO-TRIS-σ-HOMOBENZENES AS TRIDENTATE LIGANDS - X-RAY CRYSTAL.
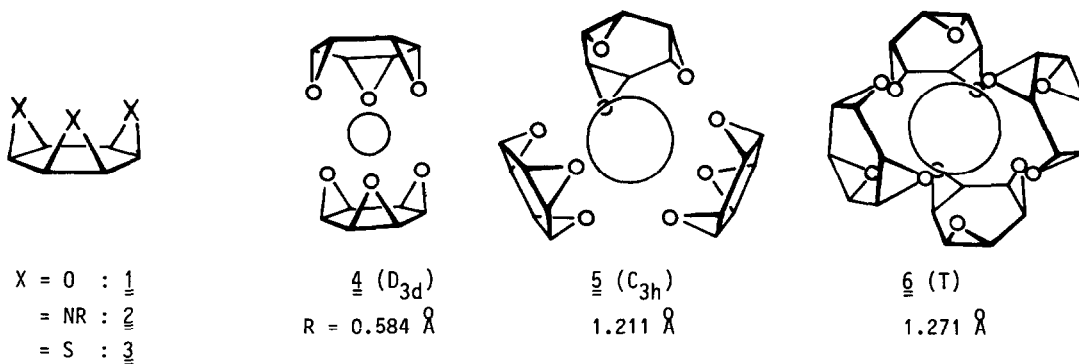
STRUCTURE ANALYSES OF THE $Co(C_6H_9N_3)_2(NO_3)_3$ and $Ba(C_6H_6O_3)_4(ClO_4)_2$-COMPLEXES

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According to X-ray crystal structure analyses "cis-benzenetrisimine"($\underline{2}$) and "cis-benzenetrioxide"($\underline{1}$) act as tridentate ligands in their 2:1- and 4:1-complexes $\underline{7}$ ($Co(C_6H_9N_3)_2(NO_3)_3$) and $\underline{8}$ ($Ba(C_6H_6O_3)_4(ClO_4)_2$), resp. The latter is the rare example of an organic complex with the (approximate) T-symmetry.

The ability of the cis-trioxa-($\underline{1}$)-[1], cis-triaza-($\underline{2}$)-[2] and cis-trithia-tris-σ-homobenzenes ($\underline{3}$)[3] - as well as of their "mixed" analogues [2,4] - to form complexes with electrophilic partners is of stereochemical and preparative interest particularly in its consequences for the [2+2+2]-cycloreversion, the substitution reactions, separation and isolation. As ligands of the crown-ether type [5] these tris-σ-homobenzenes have obvious steric and entropic/enthalpic advantages (restricted steric demand, inflexibility of the skeleton, high dipole moment) as well as disadvantages (relatively weak electron donor quality [6] and in the case of $\underline{1}/\underline{3}$

X = O : $\underline{1}$

= NR : $\underline{2}$

= S : $\underline{3}$

$\underline{4}$ (D_{3d})

R = 0.584 Å

$\underline{5}$ (C_{3h})

1.211 Å

$\underline{6}$ (T)

1.271 Å

limited n-electron participation), the relative importance of which was a priori not clear.

Estimates concerning the possible types of complexes with these tris-σ-homobenzenes as tridentate ligands were made for the complexes with two ($\underline{4}$), three ($\underline{5}$) and four ($\underline{6}$) $C_6H_6O_3$-

ligands [7]. The minimal ionic radii R were calculated on the assumption that the O-O dis-
tance in $\underline{1}$ (2.818 Å) [8] also limits the intermolecular distances. It is understood, however,
that the cation-oxygen distances can be considerably larger than the sum of the van der
Waals radii [9]. From these models it became apparent that because of the specific geometry
of $\underline{1}(\underline{2}/\underline{3})$high coordination free from drastic steric constraints should be possible. By a sui-
table selection of medium and anion it has been possible to isolate crystalline complexes of
uni- and bivalent main group elements with one (CsI), with two (Li, K, Rb, Cs as permangana-
tes ; Li as perchlorate, Li, Na, K, Rb as iodides, Li as bromide), with three $(Ca(ClO_4)_2)$and
with four molecules of $\underline{1}$ (Sr, Ba as perchlorates, permanganates, Ba as tetrafluoroborate),
as predicted. All complexes between trisimine $\underline{2}$ (R=H) [2] and elements of the first and second
main group as well as of the first sub group that have been characterised are of the 2:1
type, with the exception of the $Ba(ClO_4)_2$-complex (3:1) [10]. There are indications that $\underline{2}$
(R=H) forms a 4:1 complex with La $(ClO_4)_3$ [11]. Common features of the main group complexes
are their high thermal stability as crystals and their instability in solution. In fact, ac-
cording to NMR-and osmometric measurements, no significant interactions in solution exist.
The complexes with the N,N',N''-trimethyl-trisimine $\underline{2}$ (R=CH_3) are somewhat more stable ; e.g.,
the 2:1-complex with sodium methanosulfonate can be extracted with water from its CH_2Cl_2-
solution, and a stable 1:1-complex with $CHCl_3$ has been reported [2].

X-ray structural analyses of $Co(C_6H_9N_3)_2(NO_3)_3$ ($\underline{7}$) [12] and of $Ba(C_6H_6O_3)_4(ClO_4)_2$ ($\underline{8}$) [13]
establish that $\underline{1}$ and $\underline{2}$ act as tridentate ligands, according to the coordination types postu-
lated in $\underline{4}$ and $\underline{6}$.

In Fig.1 the geometrical details of $\underline{7}$ and space filling models [14] of the central CoN_6-
part and of the whole complex are shown. As a consequence of the space group symmetry (Pnnm,
Z=2) the cation shows exact C_{2h}(2/m) symmetry. The central Co-atom is surrounded by two mole-

Fig. 1 $\underline{7}$ $\boxed{Co(C_6H_9N_3)_2(NO_3)_3}$
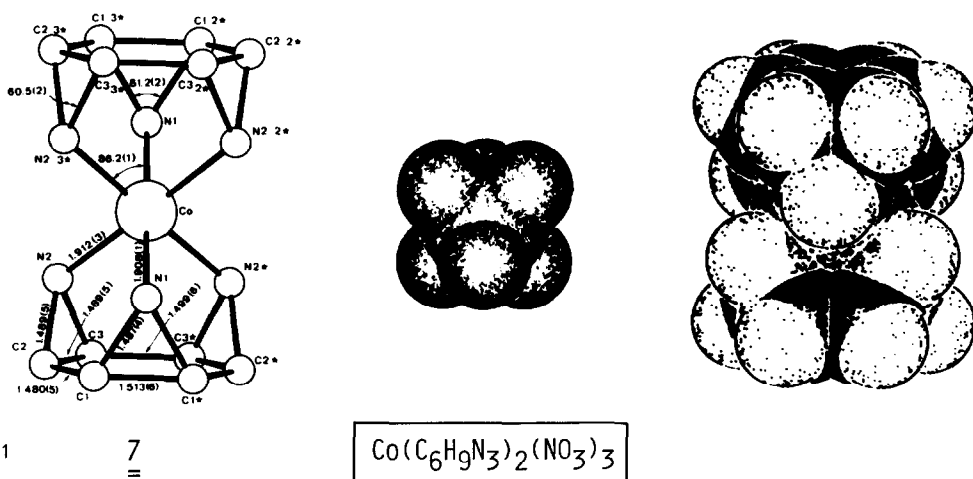
cules of tridentate $\underline{2}$ with the six nitrogen atoms lying at the corners of an octahedron. The
resulting Co-N distances are 1.909(1) Å (axial) and 1.913(3) Å (equatorial). This closely
corresponds to the mean Co-N distance 1.923(5) Å found for a topologically similar Co^{3+}-com-

plex [15]. In comparing the structural details of the trisimine ligands with the reported struc
ture of 2 (R=H) [16], the following points are noteworthy. The C-C bond lengths in the aziri-
dine units are not significantly shortened upon complexation (see the prediction for proto-
nation [17]). The interplanar angles of 100° (equatorial and axial) formed by the three azi-
ridine rings with the now planar (± 0.002 Å) six-membered ring are significantly smaller
(103.77°, 112.4°, 113.06° in 2) and, consequently, the intramolecular N-N distances within
one cage (av. 2.612 Å which is only slightly shorter than the distances to the equivalent
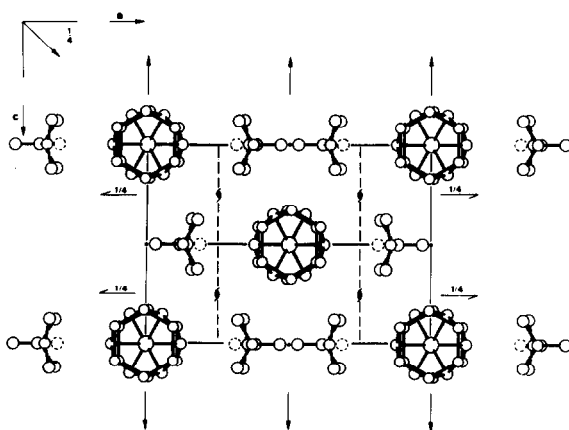N-atoms of the second cage (2.790 Å)) are clearly shorter (2.916 and 3.134 Å in 2 (R=H)).

Fig.2 presents the coordination geometry of 8 and space filling models [14] of the central
BaO_{12}-part and of the whole complex, the latter convincingly demonstrating the steric advan-
tages of 1 as a tridentate ligand. 8 is the rare example of an organic complex with (approxi-
mate) T-symmetry [18]. Each barium atom is surrounded by twelve oxygen atoms. The coordination
polyhedron is an "irregular" icosahedron, Ba-O distances range from 2.811 to 2.887 Å, only
slightly exceeding the sum of the ionic radius of barium (1.35 Å) and van der Waals radius of
oxygen. Even more than in 7 the geometrical details of the ligands resemble those of the un-
complexed molecule [8]. Specifically, the C-C bond lengths of the epoxide units (av. 1.466 Å)

Fig. 2   8 $Ba(C_6H_6O_3)_4(ClO_4)_2$
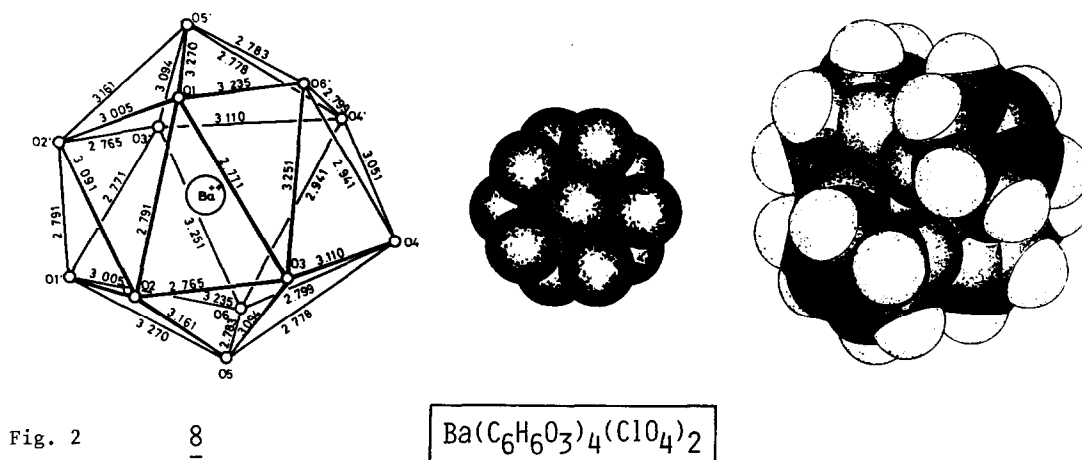
and the dihedral angles between the six-membered and the three-membered rings (av. 104.9°) as
well as the O-O distances (av. 2.781 Å) are only slightly changed by the complexation (1.470
Å, 106.9°, 2.823 Å in 1). The O-O distances between adjacent oxygen atoms of different 1-
units are somewhat larger (2.941 to 3.270 Å) causing the distortion of the icosahedron and
producing four triangles with three long sides, four with three shorter almost equal sides
and twelve with two long sides and one short one. Similar twelve-coordinate complexes of rare
earth metals (Ce, Th, Pr) with nitrate [19] and 1,8-naphtyridine [20] as bidentate O- and N-
ligands have been reported. As demanded by the symmetry of the lattice a 1:1 ratio of the
two enantiomeric forms of 8 is observed [13].

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12) Details of the structural analysis as well as atomic parameters and structure factors have been deposited. Information may be obtained from Fachinformationszentrum Energie-Physik-Mathematik, D-7514 Eggenstein-Leopoldshafen, BRD, on submission of the supplementary publication No 50149, the name of the authors and the literature reference.

Fig. 3
Projection of the contents of one unit cell upon the ac plane. One molecule of water statistically occupies the site of a nitrate group (dotted circles).

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