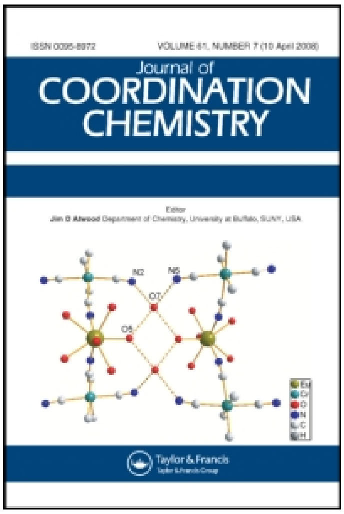

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# THE CRYSTAL AND MOLECULAR STRUCTURE OF IODO(TRIETHYLENETETRAMINE) ZINC(II) IODIDE

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# THE CRYSTAL AND MOLECULAR STRUCTURE OF IODO(TRIETHYLENETETRAMINE) ZINC(II) IODIDE*

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Crystals of [Zn(trien)I]I (trien = triethylenetetramine $C_6N_4H_{18}$) are orthorhombic. The space group is $P2_12_12_1$, with four molecules in the unit cell of dimensions $a = 11.97(1)$, $b = 13.72(1)$, $c = 8.12(1)$Å. A total of 2029 independent reflections was measured with a Siemens A.E.D. automatic diffractometer using $MoK_\alpha$ radiation. The structure was refined by full-matrix least-squares to a conventional $R$ factor of 0.041 for 1435 observed reflections. The coordination around the central zinc atom is square pyramidal with the zinc atom 0.71 Å above the plane of the four nitrogen atoms of the ligand molecule. The values of coordination bond lengths, Zn–N(prim) 2.13 Å, Zn–N(sec) 2.19 Å, Zn–I 2.59 Å fall all in the range expected for covalent bonds. The molecular structure is discussed in comparison with that of [Cu(trien)SCN]CNS.

Structural investigations on complexes of some transition elements of the first row with $\beta$-$\beta'$-$\beta''$ triaminotriethylamine (tren) and its linear isomer triethylenetetramine(trien) give clear evidence on the influence that the ligand or the metal play in determining the geometry of the coordination polyhedron.

In the case of "tren", X-ray structural investigations have shown a distorted octahedral geometry for $Ni(tren)(NCS)_2$[2] and a trigonal bipyramidal one for [Cu(tren)NCS]SCN[3] and [Zn(tren)NCS]SCN.[4] The compound $Ni(trien)(ClO_4)_2$ is planar,[5] while $Ni(trien)(NCS)_2$ is, as its homologous tren, approximately octahedral;[6] octahedral geometry has also been found in several (Co(III)trien) complexes[7, 8, 9, 10]. The compound [Cu(trien)SCN]SCN[11] has, differently from the "tren" derivatives, a square pyramidal configuration with the four "trien" nitrogen atoms on the basal plane and the thiocyanate sulphur atom on the apex of the pyramid.

With the aim of giving additional information on this series of compounds, we undertook an X-ray analysis of $Zn(trien)^{++}$. Unfortunately, this complex could be obtained in a form suitable for a single crystal study only as the diiodide salt. The large contributions by the iodine atoms to X-ray scattering reduce the precision with which the parameters of the lighter atoms can be determined, but do not undermine the possibility of finding the overall structural features, which was the main objective of this study.

## EXPERIMENTAL

The compound $Zn(trien)I_2$ was prepared by adding to an aqueous solution of $ZnI_2$ a slight stoichiometric excess of trien. The precipitate was filtered and washed with ethyl alcohol; recrystallization from water gave colourless prisms elongated along *c*. A crystal of dimensions 0.10 × 0.18 × 0.27 mm parallel to *a*, *b* and *c* respectively was selected and mounted along the *c* axis. Oscillation and equi-inclination Weissenberg photographs showed the crystals to be orthorhombic; systematic absences observed for the odd orders of *h00*, *0k0* and *00l* are consistent with the space group $P2_12_12_1$. The cell constants and their estimated standard deviations were obtained by a least squares fit to $(\theta,\chi,\phi)_{hkl}$ values of 15 reflections measured at 20°C on a Siemens single-crystal diffractometer using $MoK_\alpha$ radiation ($\lambda = 0.71069$ Å). The final values, with standard deviation in parentheses, are $a = 11.97(1)$, $b = 13.72(1)$, $c = 8.12(1)$; cell volume = 1333.2Å$^3$. The density, determined picnometrically as 2.30 ($\pm$0.03) g/cm$^{-3}$ agrees satisfactorily with that calculated, 2.32 g/cm$^{-3}$ for four formula units per cell.

The crystal was mounted with the *c* axis parallel to the $\phi$ axis of a Siemens single-crystal diffracto-

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* This paper was presented at the Eighth International Congress of the International Union of Crystallography, Stony Brook (N.Y.), U.S.A., 7–24 August, 1969.[1]

meter, equipped with a pulse height analyzer. The data were collected with Zr-filtered MoK$_\alpha$ radiation using the $\omega$–$2\theta$ scan method; all reflections (2029) in one octant of the reciprocal lattice up to $2\theta = 58°$, were measured. The reflections (484) whose intensities were less than twice their standard deviation ($\sigma^2(\mathrm{I})$ = total (peak + background) counts + $(0.01 \times \text{intensity})^2$) were coded as "unobserved" and assigned an effective intensity of $\mathrm{I} + 2\sigma_\mathrm{I}$. Lorentz and polarization factors were applied to all intensities and the structure factor was calculated for each reflection. The linear absorption coefficient for MoK$_\alpha$ radiation is 65.36 cm$^{-1}$; no correction was applied for its effects.

## STRUCTURE REFINEMENT

Refinement was carried out by the full-matrix least-squares ORFLS program as adapted by Stewart[12] starting from the atomic parameters obtained by photographic data,[1] and by assigning unit weights to all observed reflections. (Unobserved reflections were given zero weight in these and subsequent cycles). The function minimized was $\Sigma w(k|Fo| - |Fc|)^2$. The atomic scattering factors used were those of Cromer and Waber,[13] for I, Zn, N and C and those of Stewart, Davidson and Simpson,[14] for hydrogen. Two cycles with individual isotropic temperature factors reduced $R = \dfrac{\Sigma\,|Fo| - |Fc|}{\Sigma\, Fo}$ to 0.076. Two more cycles introducing anisotropic thermal parameters for iodine and zinc atoms reduced $R$ to 0.048. Then a three-dimensional difference Fourier synthesis was computed. Although there were peaks at the positions expected for some of the hydrogen atoms, they were generally smeared and, moreover, of the same height as some other peaks which appeared in the map. Hydrogen atoms were then introduced and held fixed at calculated positions with a B value equal to 4.0 Å$^2$; two more least-squares cycles were performed using weights equal to 1 for $Fo < 3$ Fomin and $\dfrac{3\,Fo\min}{Fo}$ for $Fo > 3$ Fomin. (Fomin = 13.0), and R factor reduced to 0.045. At this point 100 reflections which were barely above the $2\sigma$ cut-off and whose $F_\mathrm{cal}$ was rather low were coded unobserved; 11 more observed reflections were also excluded from the refinement because of the large discrepancy between observed and calculated structure factors. The refinement was stopped after two more cycles which reduced the $R$-factor to 0.041 for 1434 observed reflections. The final atomic parameters and their standard deviations are given in Table I and Table II.

TABLE I

Fractional atomic positional parameters and isotropic thermal parameters. Estimated standard deviations in parentheses refer to last decimal places.

| Atom | $x$ | $y$ | $z$ | $B$ |
|---|---|---|---|---|
| $I_2$ | 0.5452(1) | −0.1502(1) | 0.1374(1) | [a] |
| $I_1$ | 0.2994(1) | −0.1005(1) | 0.7124(1) | [a] |
| Zn | 0.4036(1) | 0.0630(1) | 0.6738(2) | [a] |
| $N_4$ | 0.2882(9) | 0.1772(7) | 0.6253(13) | 3.10(16) |
| $N_5$ | 0.4174(8) | 0.1397(7) | 0.9061(12) | 2.89(15) |
| $N_6$ | 0.5780(9) | 0.0291(7) | 0.7440(13) | 3.29(18) |
| $N_7$ | 0.4808(9) | 0.0707(8) | 0.4359(14) | 3.56(18) |
| $C_8$ | 0.2741(10) | 0.2363(9) | 0.7800(17) | 3.38(20) |
| $C_9$ | 0.3809(10) | 0.2391(9) | 0.8747(16) | 3.19(20) |
| $C_{10}$ | 0.5324(11) | 0.1312(9) | 0.9714(16) | 3.40(21) |
| $C_{11}$ | 0.6131(10) | 0.1140(9) | 0.8359(17) | 3.39(21) |
| $C_{12}$ | 0.6412(12) | 0.0126(10) | 0.5887(18) | 3.91(24) |
| $C_{13}$ | 0.6018(13) | 0.0755(10) | 0.4520(19) | 4.08(25) |

[a] Treated anisotropically. See table II.

TABLE II

Iodine and zinc anisotropic temperature factors. Estimated standard deviations in parentheses refer to last decimal places. The temperature factor is of the form:

$$\exp -(\beta_{11}h^2 + \beta_{22}k^2 + \beta_{33}l^2 + 2\beta_{12}hk + 2\beta_{13}hl + 2\beta_{23}kl)$$

| | $\beta_{11}$ | $\beta_{22}$ | $\beta_{33}$ | $\beta_{12}$ | $\beta_{13}$ | $\beta_{23}$ |
|---|---|---|---|---|---|---|
| $I_2$ | 0.00718(7) | 0.00403(4) | 0.01617(15) | −0.00020(4) | −0.00007(8) | −0.00049(7) |
| $I_1$ | 0.00600(5) | 0.00362(3) | 0.01257(12) | −0.00139(4) | −0.00089(7) | 0.00052(6) |
| Zn | 0.00389(7) | 0.00283(5) | 0.00970(18) | −0.00035(5) | 0.00023(10) | −0.00032(8) |

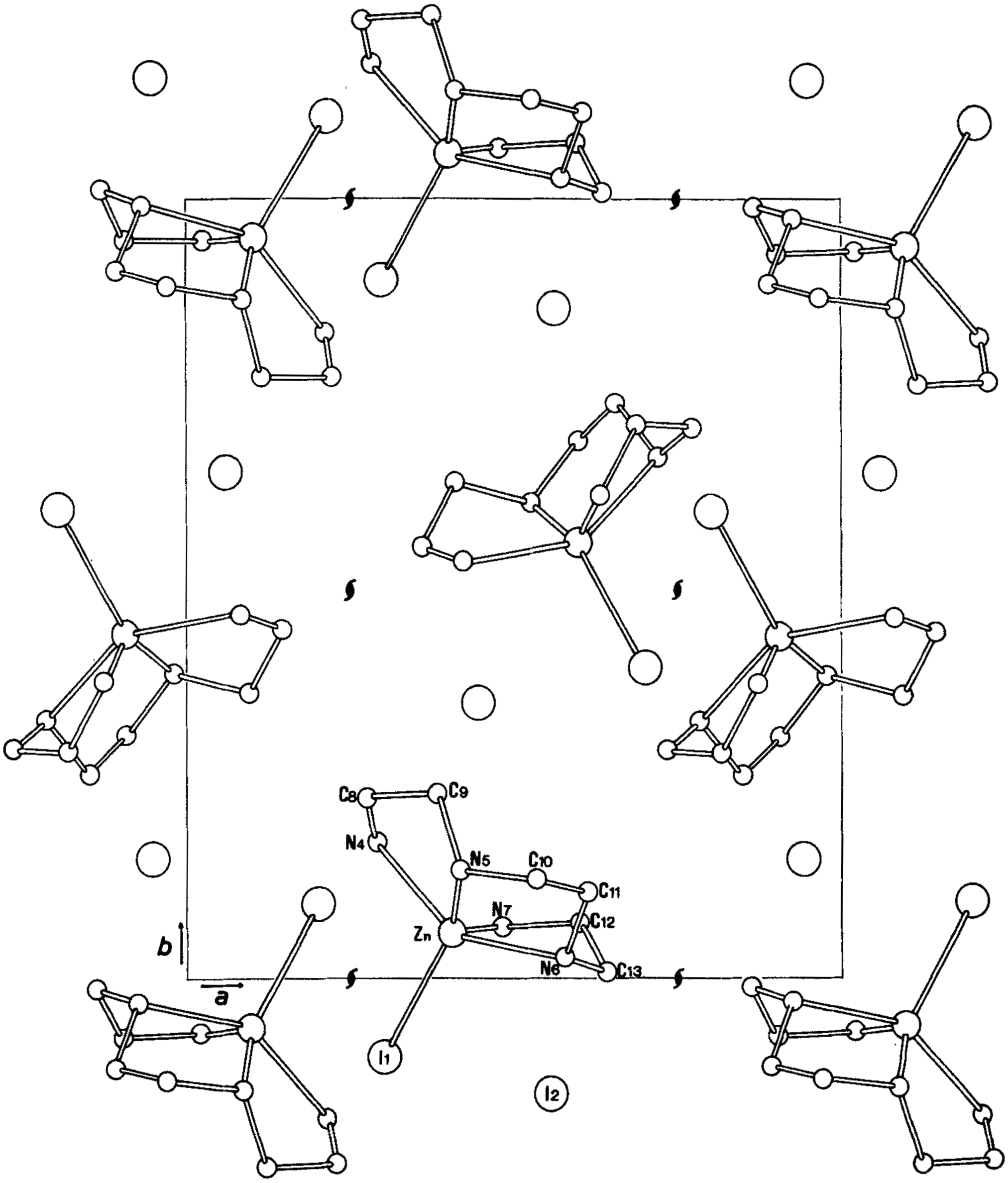


FIGURE 1 Projection of the crystal structure along *c* axis.

## DISCUSSION

The crystal structure, whose projection along the *c* axis is given in Figure 1, consists of $[\mathrm{Zn(trien)I}]^+$ cations and $\mathrm{I}^-$ anions. The cations form a sort of coil around the two fold screw axes parallel to *c*; the closest intermolecular contacts are between I(1)$(x,y,z)$ and: N(5) $(\frac{1}{2} - x,\ -y,\ -\frac{1}{2} + z)$, 3.63 Å; N(4) $(\frac{1}{2} - x,\ -y,\ \frac{1}{2} + z)$, 3.67 Å; N(7) $(\frac{1}{2} - x,\ -y,\ \frac{1}{2} + z)$, 3.83 Å. The calculated position of the hydrogen bonded to N(5) happens to be in the direction I(1) . . . . (N 5)(I(1) – H(5) – N(5) = 156°), which could be identified as a weak hydrogen bond. The anions $\mathrm{I}^-$(2) fill the positions between the coils at a distance of 4.72 Å from the Zn atom of the closest cation and form contacts with:

N(4) $(1 - x, -\frac{1}{2} + y, \frac{1}{2} - z)$, 3.76 Å;
N(7) $(1 - x, -\frac{1}{2} + y, \frac{1}{2} - z)$, 3.89 Å;
N(7) $(x,y,z)$, 3.96 Å.

Bond distances and angles in the [Zn(trien)I]$^+$ cation are given in Figure 2. The zinc ion is five coordinate, with a distorted square-pyramidal coordination polyhedron. The equation of the least-squares plane through the four amine nitrogen atoms referred to the direct cell is:
$6.253x + 11.611y - 0.842z = 3.397$. The nitrogen atoms are alternately above N(5) 0.07 Å, N(7) 0.06 Å and below N(4) − 0.06 Å, N(6) − 0.07 Å, the plane. The zinc ion is shifted by 0.71 Å towards the apical iodine I(1) and the vector Zn − I(1) is perpendicular to the basal plane. The polyhedron symmetry is close to $C_{4v}$, with a mean $I_1$-Zn-N angle of about 110°; the only one which departs significantly is the I(1)-Zn-N(6) angle, which has a value of 104°.

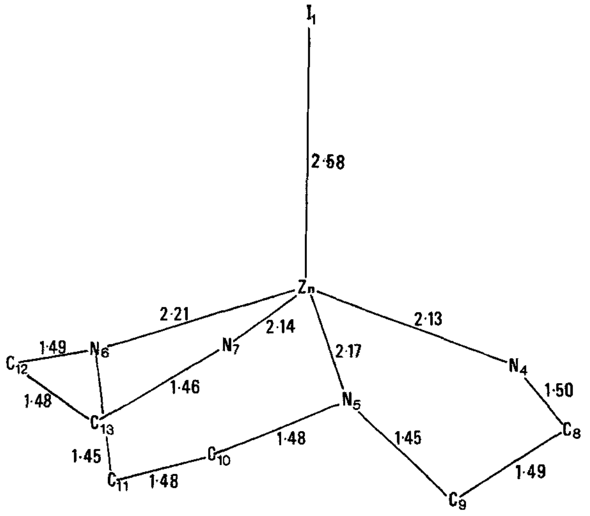


FIGURE 2a Bond distances in [Zn(trien)]I+ cation. Standard deviations are 0.01 Å for bonds involving zinc atom and 0.02 Å for C—N and C—C bonds in the ligand.

Zn—N(prim) bond distances, mean value 2.13 Å, are significantly shorter than Zn—N(sec), mean value 2.19 Å; these bonds are all to be considered rather long, as results from a comparison with the values reported in Table III. The apical Zn—I(1) bond, 2.59 Å, is closer to the value in $ZnI_2$ in the vapour state, 2.42 Å,[15] than to the sum of the ionic radii of the elements, 2.90 Å; it is almost equal to the sum of the covalent rasius of iodine, 1.33 Å, and of the $dsp^2$ radius of $Zn^{++}$, ~ 1.30 Å.[29]

The molecular parameters depart notably from those of [Cu(trien)SCN]$^+$ cation, [11] where:

(a) the apical Cu—S bond is 0.26 Å longer than the sum of the covalent radius of sulphur, 1.04 Å, and of the $dsp^2$ radius of copper(II) ion, ~ 1.30 Å;[29]
(b) the deviation of $Cu^{++}$ from the basal plane is only 0.35 Å, and therefore the pyramid is flatter;
(c) the values of Cu—N basal bonds are all equal and fall in the range reported in the literature for normal covalent bonds.[16]

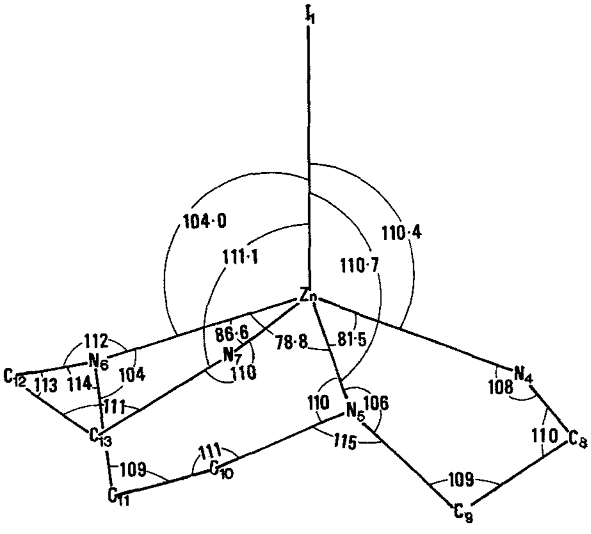


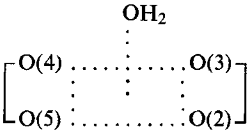
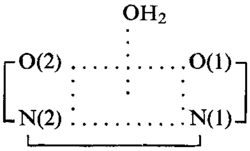
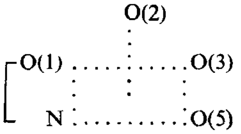
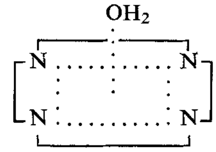
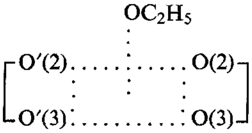
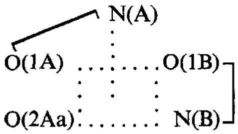
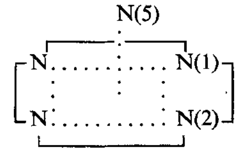
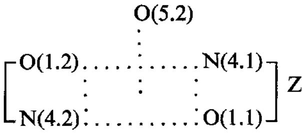
FIGURE 2b Bond angles in [Zn(trien)]I+ cation. Standard deviations are 0.4° for angles subtended at the zinc atom and 1° for angles subtended at the nitrogen and carbon atoms in the ligand.

The above mentioned differences are, in our opinion, to be ascribed to the different properties of the $Cu^{++}$ and $Zn^{++}$ ions, and can be considered systematic, as follows from the data in Table III, where the most significant parameters for the coordination polyhedron of square-pyramidal zinc complexes are reported. These data show that:

(a) in zinc complexes the apical bond is a normal coordination bond, approximately equal to the sum of covalent radii of the metal ion and of the ligand atoms, while in copper complexes the apical bond is always 0.2–0.4 Å longer than the normal covalent bonds;[16]

TABLE III

Bond distances in square pyramidal zinc complexes

| Ref. | Compound | | Apical Bond | Basal Bonds |
|---|---|---|---|---|
| 24 | Monoaquobisacetylacetonatozinc |  | Zn—$OH_2$ = 1.999 Å | Zn—O(2) = 2.026 Å<br>Zn—O(3) = 2.038 Å<br>Zn—O(4) = 2.005 Å<br>Zn—O(5) = 2.011 Å |
| 21 | *NN′*-Disalicylidine-ethylendiaminezinc(II) Monohydrate |  | Zn—$OH_2$ = 2.0 Å | Zn—O(1) = 1.9 Å<br>Zn—O(2) = 2.0 Å<br>Zn—N(1) = 2.0 Å<br>Zn—N(2) = 2.2 Å |
| 17 | Zinc glutamate dihydrate |  | Zn—O(2) = 2.030 Å | Zn—N = 2.103 Å<br>Zn—O(1) = 2.106 Å<br>Zn—O(3) = 2,036 Å<br>Zn—O(5) = 2.070 Å |
| 25 | Aquozinc(II) tetraphenylporphine |  | Zn—$OH_2$ = 2.20 Å | Zn—N = 2.05 Å |
| 26 | Bis(benzoylacetonato)zinc Monoethanolate |  | Zn—$OC_2H_5$ = 2.068 Å | Zn—O2 = 1.994 Å<br>Zn—O3 = 1.962 Å<br>Zn—O′2 = 1.998 Å<br>Zn—O′3 = 1.994 Å |
| 19 | Bis(L-serinato)zinc |  | Zn—N(A) = 2.064 Å | Zn—O(2Aa) = 1.963 Å<br>Zn—O(1B) = 2.112 Å<br>Zn—N(B) = 2.057 Å<br>Zn—O(1A) = 2.155 Å |
| 27 | α, β, γ, δ-tetra(4-pyridyl)porphinatomonopyridine zinc(II) |  | Zn—N(5) = 2.143 Å | Zn—N1 = 2.067 Å<br>Zn—N2 = 2.079 Å |
| 28 | Bis(hydrazinecarboxylato-*N′* O)-zinc |  | Zn—O(5.2) = 2.036 Å | Zn—O(1.2) = 2.058 Å<br>Zn—O(1.1) = 2.030 Å<br>Zn—N(4.1) = 2.077 Å<br>Zn—N(4.2) = 2.080 Å |

(b) the distance from the basal plane is for zinc generally higher than for copper; this happens systematically in the complexes of the two ions with the same ligand: in zinc glutamate dihydrate[17] and copper glutamate dihydrate,[18] which are isomorphous, the distances are 0.32 and 0.25 Å respectively; in bis(L-serinato)zinc[19] and bis(L-serinato)copper[20] 0.26 and 0.14 Å; in NN'disalicylidenediaminezinc(II) monohydrate[21] and disalicylideneethylendiaminecopper[22] 0.43 and 0.16 Å;

(c) the basal bonds for zinc(II) complexes are sometimes longer than the normal covalent bonds; this lengthening, which falls in the range 0.1–0.2 Å is not however systematic.

The above mentioned differences in five-coordinate square-pyramidal complexes of zinc(II) and copper(II) arise in our opinion from the $d^{10}$ configuration of the first, which favours the equivalence of basal and apical bonds; due to this equivalence, the intramolecular contacts between the apical and basal atoms in the polyhedron would shorten unless the zinc atom shifted towards the apex or the basal bonds lengthened. The first of these two effects is energetically preferred and structural data seem to confirm it. In the case of $[Zn(trien)I]^+$ this shift is the highest observed up to now, certainly as a consequence of the steric hindrance of iodine, which is likely to explain also the lengthening of basal bonds.

This lengthening is accompanied by a decrease in the angles subtended at the Zn atom by the trien chelate rings. As shown by the data in Table IV, this is a general trend in M(trien) complexes, where to a lengthening of M—N bonds corresponds a decrease in N-M-N angles; in this way the intramolecular distances between the nitrogens bridged by carbon atoms, although they lengthen with M-N distance, they keep within the range 2.65–2.80 Å, which corresponds approximately to twice the van der Waals radius of nitrogen.

Zn(trien) moiety has an RS configuration;[23] as in [Cu(trien)SCN] CNS and $Ni(trien)(ClO_4)_2$ the central ring adopts an unsymmetrical envelope conformation and the two outer chelate rings an unsymmetrical skew; however, unlike Cu and Ni compounds, these rings have all $\lambda$ conformation.

This work was supported by Italian Consiglio Nazionale delle Ricerche. The computations were performed on the IBM 1130 of the Centro di Calcolo, University of Cagliari, and on the IBM 7090, of CNUCE, Pisa.

We wish to thank Prof. P. Paoletti for suggesting this problem and Prof. L. Cavalca and M. Nardelli for the opportunity to collect the data in their laboratory.

TABLE IV

M—N bonds, N. . . . . N intramolecular distances between nitrogens bridged by carbon atoms and N—M—N intrachelate angles in some "trien" complexes

| Ref. | Compound | M—N | N. . . . N | N—M—N |
|---|---|---|---|---|
| 5 | $Ni(trien)(ClO_4)$ | 1.90 Å | 2.63 Å | 87.5° |
| 7 | *cis*-$\beta$-$(Co(trien)ClOH_2)(ClO_4)_2$ | 1.93 Å | 2.63 Å | 86.4° |
| 8 | *cis*-$\alpha$-$(Co(trien)NH_3Cl)(NO_3)_2$ | 1.96 Å | 2.68 Å | 85.9° |
| 11 | (Cu(trien)SCN)(NCS) | 2.01 Å | 2.71 Å | 84.5° |
| 2 | $Ni(trien)(NCS)_2$ | 2.13 Å | 2.77 Å | 82° |
|  | (Zn(trien)I)I | 2.13 Å | 2.80 Å | 80.3° |

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