during hydrolysis (Table V) shows that all products other than $[Co(en)_2gly]^{2+}$ have consumed 2 equiv of OH^-, and columns 3 and 6 of Table V show that base consumption can occur before, during, and after the k_1 path. For example small amounts of *cis*- and *trans*-$[Co(en)_2(OH)(glyO)]^+$ were formed from the chloro

$$[Co(en)_2Cl(glyOR)]^{2+} + OH^- \longrightarrow [Co(en)_2Cl(glyO)]^+ + ROH$$

$$[Co(en)_2Cl(glyO)]^+ + OH^- \longrightarrow [Co(en)_2(OH)(glyO)]^+ + Cl^-$$

esters. Also, it is evident from the agreement between columns 5 and 6, for $[Co(en)_2Br(glyOCH(CH_3)_2)]^{2+}$ (Table V), that the ~27% of other products results from reactions occurring after loss of Br^- (k_1). For the other halo esters the side products form both before and after loss of halide.

Acknowledgments. The authors wish to thank the microanalytical units of the John Curtin School of Medical Research and the Research School of Chemistry, Australian National University, for N, C, H, and Co analyses, Dr. F. Bergerson and Mr. G. Turner of the CSIRO Division of Plant Industry for the isotope ratio measurements, and Dr. G. Johnston of the John Curtin School for the gas chromatographic measurements.

The Crystal Structure of β,β′,β″-Triaminotriethylamineisothiocyanatozinc(II) Thiocyanate[1]

G. D. Andreetti,[2] Prem C. Jain,[3] and E. C. Lingafelter

Contribution from the Department of Chemistry, University of Washington, Seattle, Washington 98105. *Received February 13, 1969*

Abstract: The crystal structure of β,β′,β″-triaminotriethylamineisothiocyanatozinc(II) thiocyanate, [Zn(tren)-(NCS)](SCN), has been determined by Fourier methods and refined by full-matrix least squares using three-dimensional X-ray data consisting of 2561 independent reflections measured with Mo Kα radiation on a four-circle diffractometer by the ω–2θ scan technique. The final values of R and R_w are 0.054 and 0.038, respectively. The crystals have space group Pbca and a cell of dimensions a = 12.888, b = 16.466, c = 13.633 Å containing eight molecules. Calculated and measured densities are 1.504 and 1.49 g cm^{-3}, respectively. The crystal structure consists of trigonal-bipyramidal $[(tren)(SCN)Zn]^+$ cations and SCN^- anions, connected by a network of NH · · · N and NH · · · S hydrogen bonds.

The structures of the complexes of the polyamine ligand, β,β′,β″-triaminotriethylamine ($N(CH_2CH_2NH_2)_3$ ≡ tren) with bivalent metal ions are of considerable interest. X-Ray crystallographic studies of the solids have shown that $Ni(tren)(NCS)_2$[4] has a six-coordinate *cis*-octahedral structure, while the copper(II)[5] and zinc(II)[1] compounds have a five-coordinate trigonal-bipyramidal structure. Thermodynamic, conductometric, and spectral studies of solutions suggest[6] that the manganese(II) and iron(II) compounds are probably six-coordinate and the cobalt(II) compound is five-coordinate.

A study of the complexes of tris(2-dimethylaminoethyl)amine with the bivalent metal bromides of Mn, Fe, Co, Ni, Cu, and Zn has shown the six compounds to be isomorphous and to consist of trigonal-bipyramidal $MLBr^+$ cations and bromide anions.[7-9]

We report here the details of the X-ray crystallographic study of the zinc compound, [Zn(tren)-(NCS)](SCN).

Experimental Section

[Zn(tren)(NCS)](SCN) was prepared from aqueous solution by the method of Barclay and Barnard[10] and recrystallized from water.

A colorless crystal of dimensions 0.28 × 0.16 × 0.16 mm was selected for study. Oscillation and equiinclination Weissenberg photographs showed the crystal to be orthorhombic. Systematic absence of 0*kl* for $k \neq 2n$, *h*0*l* for $l \neq 2n$, and *hk*0 for $h \neq 2n$ indicate the space group Pbca. The lattice parameters were determined using Mo Kα radiation (λ 0.71069 Å) from the least-squares fit to measurements of 22 θ values in the range 13–21° (determined by the +2θ, −2θ technique), taken on a Picker single-crystal diffractometer at 24°.

Crystal Data. The lattice parameters are $a = 12.888 \pm 0.002$, $b = 16.466 \pm 0.003$, $c = 13.633 \pm 0.002$ Å; cell volume 2893.1 Å.^{3} The density measured by the flotation method, 1.49 g cm^{-3}, agrees satisfactorily with that calculated, 1.504 g cm^{-3}, for eight formula units per cell. $F(000) = 1360$. The linear absorption coefficient for Mo Kα radiation is 20.1 cm^{-1}.

The crystal was mounted with the a axis parallel to the φ axis of a Picker automated single-crystal diffractometer equipped with a pulse-height analyzer. Intensity data were collected using Mo Kα radiation. Diffractometer settings for each possible reflection with all indices positive for the ω–2θ scan method were calculated using

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Table I. Positional Parameters ($\times 10^4$) and Thermal Parameters ($\times 10^2$)

Atom	x/a	y/b	z/c	B_{11}	B_{22}	B_{33}	B_{12}	B_{13}	B_{23}
Zn	2199 (1)	1874 (1)	960 (1)	335 (4)	408 (4)	403 (4)	15 (4)	28 (3)	−57 (4)
S(1)	167 (1)	3893 (1)	2578 (1)	477 (9)	463 (9)	611 (10)	52 (7)	167 (9)	−24 (9)
S(2)	4306 (2)	3778 (2)	−448 (2)	519 (12)	1594 (26)	1380 (25)	159 (16)	70 (15)	474 (21)
N(1)	3278 (4)	852 (3)	448 (4)	446 (26)	316 (24)	460 (27)	82 (21)	35 (24)	4 (23)
N(2)	3608 (5)	2335 (4)	1429 (5)	480 (31)	608 (41)	764 (44)	−133 (29)	−49 (34)	−222 (36)
N(3)	1551 (5)	935 (5)	1748 (5)	456 (31)	809 (44)	527 (34)	−107 (33)	104 (29)	136 (35)
N(4)	1872 (5)	1893 (4)	−508 (5)	436 (28)	550 (38)	445 (30)	60 (31)	−50 (24)	28 (29)
N(5)	1300 (4)	2805 (4)	1469 (4)	570 (31)	622 (36)	679 (38)	154 (28)	61 (30)	−153 (30)
N(6)	2464 (9)	3573 (6)	−1358 (6)	1526 (84)	863 (94)	1039 (64)	−350 (60)	−390 (63)	222 (48)
C(1)	4335 (6)	1124 (5)	622 (8)	285 (34)	755 (56)	1203 (78)	6 (35)	85 (43)	−186 (55)
C(2)	4445 (6)	1739 (6)	1395 (6)	378 (35)	872 (63)	775 (54)	95 (41)	−181 (39)	−203 (48)
C(3)	2990 (8)	127 (5)	1013 (8)	676 (51)	467 (41)	981 (63)	141 (38)	125 (49)	291 (45)
C(4)	1943 (13)	171 (6)	1438 (10)	1668 (125)	485 (55)	1349 (110)	−435 (66)	620 (98)	192 (60)
C(5)	3039 (9)	741 (6)	−589 (8)	1179 (89)	663 (58)	422 (39)	386 (58)	75 (54)	−98 (39)
C(6)	2652 (9)	1438 (9)	−1061 (6)	839 (59)	1239 (75)	372 (39)	450 (58)	−113 (48)	−144 (54)
C(7)	824 (5)	3250 (4)	1917 (4)	351 (27)	443 (33)	423 (31)	−49 (26)	9 (25)	13 (28)
C(8)	3527 (8)	3655 (5)	−1002 (6)	1191 (75)	413 (39)	513 (45)	−81 (49)	126 (51)	−6 (38)
Positional Parameters ($\times 10^3$) and Isotropic Thermal Parameter ($\times 10^1$)									
H(11)	481 (5)	58 (4)	95 (5)	85 (6)					
H(12)	465 (6)	148 (5)	−23 (6)	115 (10)					
H(21)	520 (5)	201 (4)	151 (5)	63 (5)					
H(22)	430 (5)	126 (4)	208 (5)	85 (6)					
H(31)	345 (5)	−34 (4)	71 (5)	85 (6)					
H(32)	331 (5)	28 (4)	198 (5)	85 (6)					
H(41)	194 (6)	−11 (5)	196 (5)	84 (6)					
H(42)	144 (6)	−13 (5)	96 (6)	85 (6)					
H(51)	374 (5)	49 (4)	−90 (5)	69 (5)					
H(52)	250 (8)	50 (6)	−64 (8)	99 (10)					
H(61)	250 (8)	145 (6)	−151 (5)	75 (6)					
H(62)	348 (6)	181 (4)	−92 (5)	85 (6)					
H(221)	397 (6)	265 (5)	102 (6)	116 (10)					
H(222)	356 (6)	224 (5)	216 (5)	98 (10)					
H(331)	174 (5)	104 (4)	245 (5)	71 (6)					
H(332)	65 (6)	91 (5)	179 (5)	99 (10)					
H(441)	106 (5)	165 (4)	−67 (4)	58 (5)					
H(442)	181 (6)	223 (4)	−71 (6)	51 (5)					

The thermal parameters are of the form $\exp\left(-\frac{1}{4}\sum_{i=1}^{3}\sum_{j=1}^{3}B_{ij}h_ih_ja_i{}^*a_j{}^*\right)$

the formula of Alexander and Smith:[11] scan range = $A + B \tan \theta$, with $A = 0.90°$ and $B = 1.0°$. Background counts were taken at each end of the scan range for preset times approximately equal to one-half of the scan time and were adjusted to exactly one-half of the scan time during data reduction. Reflections in the range $0 < 2\theta \leq 45°$ were scanned at 2°/min; those in the range $45° < 2\theta \leq 50°$, at 1°/min. At 4-hr intervals during the data-collection period, a set of four standard reflections was remeasured. The scale factors calculated from these standard reflections showed a maximum variation of ±1%. A coincidence counting loss correction was applied in the form $I_{\text{cor}} = I_{\text{obsd}}/(1 - I_{\text{obsd}}\tau)$, with τ empirically determined to be 10^{-7}. The maximum correction was below 0.2%.

In order to estimate standard deviations of the measured intensities, the usual assumption was made that σ is a function of intensity only. A set of eight reflections was selected covering the range of intensity, and the intensity of each reflection was measured 25 times. From the 25 measurements for each reflection, an empirical standard deviation was calculated. These empirical standard deviations gave a satisfactory straight line when plotted against $\sqrt{I}$: $\sigma(I) = 0.090 + 0.399\sqrt{I}$. This expression was therefore used to calculate the standard deviation of the intensity for each reflection measured. Each reflection for which the measured intensity was less than twice its standard deviation was coded as an "unobserved" reflection, so that its contribution could be omitted during any least-squares refinement cycle for which the calculated structure factor was less than the observed structure factor. Of the total of 2561 independent reflections measured, 751 were coded as "unobserved." Lorentz and polarization factors were applied and the structure factor and its standard deviation were calculated for each reflection.

Structure Determination. A three-dimensional Patterson synthesis clearly showed the position of the zinc atoms. On a Fourier synthesis calculated with phases determined by the zinc atoms, it was possible to assign the positions of one sulfur atom and ten light atoms. A second Fourier synthesis showed all of the nonhydrogen atoms in positions which gave $R = 0.23$. (R is defined as $\Sigma||F_o| - |F_c||/\Sigma|F_o|$, summed over the unique observed reflections.) Refinement was carried out by full-matrix least squares, minimizing $\Sigma w(F_o - F_c)^2$, using the X-RAY 63 system.[12] The atomic scattering factors used were those from the "International Tables for X-Ray Crystallography" for zinc,[13] those of Berghuis, *et al.*, for nitrogen and carbon,[14] those of Viervoll and Ögrim for sulfur,[15] and those from Table II of Stewart, Davidson, and Simpson[16] for hydrogen. Four cycles of refinement of position and isotropic thermal parameters of all nonhydrogen atoms, holding the hydrogen atoms fixed in calculated positions, and with all $w = 1$, reduced R to 0.10. A difference Fourier synthesis showed all hydrogen atoms. Subsequent refinement cycles included a scale factor, positions of all atoms, anisotropic thermal parameters for nonhydrogen atoms, and isotropic thermal parameters for hydrogen atoms. Because of the large number of parameters, 227, and the limitations of core in the 7094, it was necessary to carry out the refinement in blocks. Three cycles with $w = 1$ reduced R to 0.052 and R_w to 0.048 ($R_w = [\Sigma w(F_o - F_c)^2/\Sigma w(F_o)^2]^{1/2}$). Five cycles with $w = 1/\sigma^2$ gave final values of $R = 0.054$ and $R_w = 0.038$. The estimated standard er-

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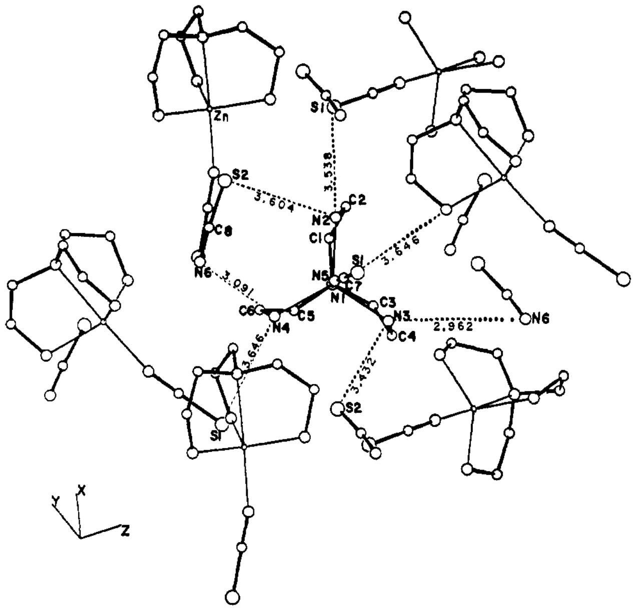

Figure 1. Partial projection of [Zn(tren)(NCS)](SCN) structure on plane normal to N_{tert}–Zn–N_{thio} line of central cation.

ror of an observation of unit weight was 2.2. In the final cycle the average parameter shift was 0.08σ and the maximum was 0.58σ. The final values of the parameters[17] and their standard deviations are listed in Table I.

Discussion

The crystal structure consists of trigonal-bipyramidal $[Zn(tren)(NCS)]^+$ cations and SCN^- anions, as found for the copper(II) compound.[5] However, the zinc and copper compounds are not isostructural. The differences between the two crystal structures are clearly shown in Figures 1 and 2 which show partial projections of the two structures on the plane perpendicular to the N(tertiary amine)–metal–N(thiocyanate) line. Both the zinc complex ion and its environment show much less distortion from threefold axial symmetry than the copper complex.

Table II. Bond Lengths (in Ångstroms) and Angles (in Degrees)

Zn-N(2) = 2.071 (5)	Zn-N(5) = 2.043 (5)
Zn-N(3) = 2.059 (6)	Zn-N(1) = 2.292 (4)
Zn-N(4) = 2.044 (6)	
N(2)-Zn-N(3) = 118.03 (0.21)	N(1)-Zn-N(2) = 80.22 (0.19)
N(2)-Zn-N(4) = 118.49 (0.22)	N(1)-Zn-N(3) = 81.63 (0.19)
N(3)-Zn-N(4) = 116.02 (0.21)	N(1)-Zn-N(4) = 80.69 (0.18)
	N(5)-Zn-N(2) = 96.74 (0.20)
N(1)-Zn-N(5) = 176.77 (0.17)	N(5)-Zn-N(3) = 98.96 (0.20)
	N(5)-Zn-N(4) = 101.81 (0.20)
N(1)-C(1) = 1.452 (8)	N(2)-C(2) = 1.459 (9)
N(1)-C(3) = 1.469 (8)	N(3)-C(4) = 1.420 (11)
N(1)-C(5) = 1.458 (9)	N(4)-C(6) = 1.463 (11)
C(1)-C(2) = 1.468 (11)	C(3)-C(4) = 1.408 (13)
C(5)-C(6) = 1.471 (15)	
N(1)-C(1)-C(2) = 114.9 (0.6)	N(2)-C(2)-C(1) = 114.5 (0.6)
N(1)-C(3)-C(4) = 113.5 (0.6)	N(3)-C(4)-C(3) = 119.2 (0.8)
N(1)-C(5)-C(6) = 114.6 (0.6)	N(4)-C(6)-C(5) = 114.6 (0.6)
C(1)-N(1)-Zn = 113.7 (0.5)	
C(3)-N(1)-Zn = 113.3 (0.6)	
C(5)-N(1)-Zn = 110.6 (0.5)	

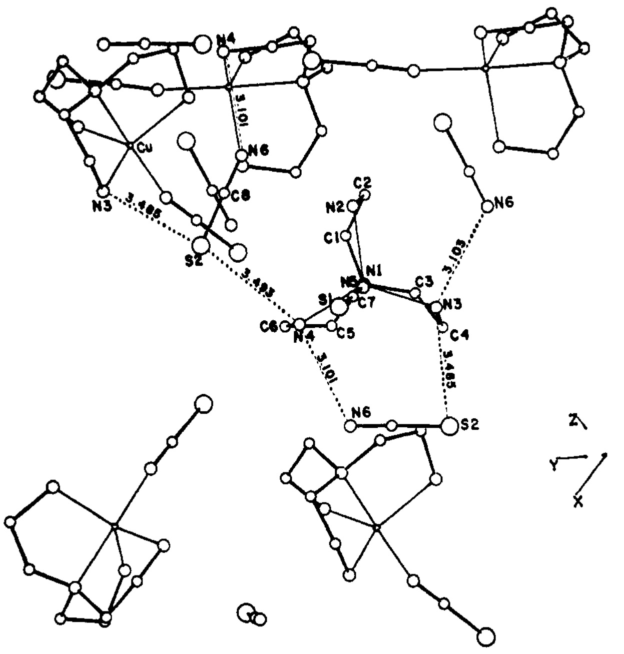

Figure 2. Partial projection of [Cu(tren)(NCS)](SCN) structure on plane normal to N_{tert}–Cu–N_{thio} line of central cation.

Bond lengths and angles are shown in Table II. The equatorial N–Zn–N angles are all within 5 standard deviations of the mean value of 117.5°. The intrachelate N–Zn–N bond angles, all three of which are equal to the mean value of 80.9° within 4 standard deviations, differ significantly from the value 84.1° in $Cu(tren)(NCS)_2$,[5] 85° in $Cu(en)_2(SCN)_2$,[18] 86° in $Cu(en)_2(NO_3)_2$,[19] and require the zinc atom to lie 0.34 Å below the equatorial plane toward the thiocyanate nitrogen atom. In $Cu(tren)(NCS)_2$[5] the metal atom is 0.22 Å out of the plane in the same direction. The equatorial Zn–N bonds are equal within four standard deviations [2.071 (5), 2.059 (6), and 2.044 (6) Å] and do not differ from the Zn–N(5) (thiocyanate) distance [2.043 (5) Å]. However, the Zn–N(1)(tertiary amine) is significantly longer [2.292 (4) Å]. Similar values have been found in $Zn(Me_6tren)Br_2$:[9] 2.11 (2) for $Zn–N_{eq}$ and 2.19 Å for $Zn–N_{apic}$. Other Zn–N distances reported in the literature for various Zn coordinations are as follows: trigonal bipyramid, 2.079 (6) Å in $C_6H_5N \cdot Zn[S_2CN(CH_3)_2]_2$,[20] 2.051 (4) and 2.064 (5) Å in $C_6H_4(O)CHNHCH_3)_2Zn$,[21] 2.18 (4) and 2.09 (4) Å for $Zn–N_{eq}$, and 2.24 (4) Å in $(C_{15}H_{11}N_3)ZnCl_2$;[22] square pyramid, 2.103 (4) Å for $Zn–N_{eq}$ in $(C_5H_7NO_4)$-$Zn \cdot 2H_2O$;[23] tetrahedron, 1.995 (11) and 2.020 (11) Å in $(C_3H_4N_2)_2ZnCl_2$;[24] octahedron, 2.16 (1), 2.18 (1),

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[17] Observed and calculated structure factors have been deposited as Document No. NAPS-00358 with the ASIS National Auxiliary Publication Service, c/o CCM Information Sciences,I nc., 22 West 34th St., New York, N. Y. 10001. A copy may be secured by citing the document number and by remitting $1.00 for microfiche or $3.00 for photocopies. Advance payment is required. Make checks or money orders payable to: ASIS–NAPS.

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and 2.19 (1) Å in $Zn(N_2H_4)_2(NCS)_2$,[25] 2.07 (1) Å in $[OC(NH_2)NHNH_2]ZnCl_2$,[26] 2.179 (7) and 2.206 (7) Å in $[Zn(N_2H_4)_3][(CH_3COO)_2]_n$,[27] and 2.099 (4) in $Zn[C_7H_6N_2O]_2 \cdot 2H_2O$.[28]

All three ethylenediamine chelate rings have the *gauche* configuration with the angles between the planes CCN(1) and N(primary)CC respectively 37.5, 33.4, and 43.6°, and all have the k conformation as in the case of $Cu(tren)(NCS)_2$[5] and of the isomorphous series $M(Me_6tren)Br_2$.[9] The asymmetry of the ethylenediamine moiety with respect to the coordination plane can most conveniently be expressed by the angle between the coordination plane defined by the metal atom and the two nitrogen atoms and the plane defined by the two nitrogen atoms and the midpoint of the carbon–carbon bond. These angles are 3.2, 3.4, and 4.9° for N(2), N(3), and N(4) chelate rings, respectively. The corresponding values in $Cu(tren)(NCS)_2$[5] are 5.6, −0.6, and 7.3°, in $Ni(tren)(NCS)_2$[2] 15.6, 25.5, and 19.3°, and 8.3° in $Co(Me_6tren)Br_2$.[7] The observed differences between lengths of chemically identical bonds in the tren molecule are possibly significant (maximum difference, 4.5σ), but we can suggest no explanation for these small differences.

The Zn–N–C (thiocyanate) angle is 166.6° and agrees with the values reported in the literature: 161.2° in $Zn(N_2H_4)_2(NCS)_2$,[27] 163.3° in $Cu(tren)(NCS)_2$.[5] In Table III are compared bond distances and angles of the thiocyanate groups found in the present work and in $Cu(tren)(NCS)_2$.[5] The C–S distances in the thiocyanate groups have been corrected for anisotropic thermal vibration effects assuming the S atom riding on the carbon atom, and the values are reported in brackets. As in the case of $Cu(tren)(NCS)_2$ the bond distances within the two thiocyanate ions are not significantly different, even though one is bonded to zinc and the other is unbonded and their infrared spectra are clearly different.[1]

Table III. Bond Lengths in Thiocyanate

		Zn(tren)	Cu(tren)
C–S, Å	Bonded	1.628 (5) [1.644]	1.612 (5)
	Unbonded	1.561 (8) [1.625]	1.624 (5)
N–C, Å	Bonded	1.135 (7)	1.142 (7)
	Unbonded	1.140 (12)	1.168 (7)
N–C–S, deg	Bonded	178.5 (0.5)	177.4 (0.5)
	Unbonded	176.1 (0.8)	178.4 (0.5)

A comparison of the general arrangement of the ions in $Zn(tren)(NCS)_2$ and in $Cu(tren)(NCS)_2$ and the hydrogen-bond network are shown in Figure 1. A list of short contacts, some of which can be considered as hydrogen bonds, is reported in Table IV. In brackets are given the H—N···atom angles.

Table IV. Short Contact Distances (Å)

N(2)–S(2)	3.604	[16.5][e]
N(2)–S(1)[a]	3.538	[61.6]
N(3)–N(6)[b]	2.962	[11.8]
N(3)–S(2)[c]	3.432	[35.5]
N(4)–S(1)[d]	3.646	[13.7]
N(4)–N(6)	3.091	[56.4]

[a] $x + {}^1/_2, y, {}^1/_2 - z$. [b] $x, {}^1/_2 - y, {}^1/_2 + z$. [c] $x - {}^1/_2, {}^1/_2 - y, z$. [d] $x, {}^1/_2 - y, z - {}^1/_2$. [e] H–N···atom angles in degrees.

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Topological Representation of Stereoisomerism. II. The Five-Atom Family[1]

E. L. Muetterties

Contribution from Frick Chemical Laboratory, Princeton University, Princeton, New Jersey 08650. *Received January 18, 1969*

Abstract: Polytopal[1] rearrangements for the five-atom family are compared by topological or matrix presentation to delineate mechanistic differences subject to experimental test in molecular species.

Stereoisomerization through polytopal[1] rearrangements is examined here on a topological basis in an attempt to identify substantive mechanistic differences for experimental tests. The topological approach and definitions were presented in the first paper of this series[1] and a later note.[2] The following discussion is limited to the five-atom family which includes five-coordinate complexes, polyhedral boranes, and metal clusters. Polytopal isomerism in this family has been extensively described in the literature, and there are pertinent general articles[3,4] and reviews.[5–7]

Polytopal Isomerism

The mechanism of intramolecular rearrangements has been generally discussed in terms of the Berry[3]

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