Table 4. *Some comparisons of distances* (Å), *angles* (°) *and torsion angles* (°) *in some lithium citrates and a glycolate*

	LiH_2 cit* (H_2 cit$^-$)	$LiNH_4$ cit (H cit^{2-})	Li_3 cit (cit^{3-})	Li glyc
C(3)—C(6)	1·55 (1)	1·541 (2)	1·545 (2)	1·525 (2)
C(1)—C(2)	1·55 (1)	1·516 (2)	1·525 (2)	—
C(4)—C(5)	1·52 (1)	1·499 (2)	1·523 (2)	—
O(5)···O(7)	2·59 (1)	2·584 (2)	2·578 (2)	2·649 (2)
C(6)—C(3)—O(7)	106 (1)	107·4 (1)	107·1 (1)	112·8 (1)
C(2)—C(3)—C(4)	111 (1)	106·0 (1)	109·4 (1)	—
O(5)—C(6)—C(3)—O(7)	−19 (2)	4·3 (2)	−19·2 (2)	7·8 (2)
C(1)—C(2)—C(3)—C(4)	56 (2)	172·1 (2)	178·1 (2)	—
C(2)—C(3)—C(4)—C(5)	158 (2)	−170·0 (2)	64·8 (2)	—

* Low accuracy, approximate e.s.d. values.

We thank Dr H. L. Carrell for many helpful discussions. This research was supported by grants CA-10925, CA-06927, RR-05539, and CA-22780 from the National Institutes of Health, US Public Health Service, BC-242 from the American Cancer Society, and by appropriation from the Commonwealth of Pennsylvania.

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Acta Cryst. (1983). C**39**, 990–993

The Structure of *a,b,c,j,k,l*-Hexaaqua-*d,e,f,g,h,i*-hexakis[μ-(4-ethyl-1,2,4-triazole-N^1,N^2)]trizinc(II) Hexakis(trifluoromethanesulphonate), $[Zn_3(C_4H_7N_3)_6(H_2O)_6][CF_3SO_3]_6$

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(*Received* 17 *March* 1983; *accepted* 4 *April* 1983)

Abstract. $M_r = 1781{\cdot}32$, trigonal, $P\bar{3}1c$, $a = 14{\cdot}450$ (2), $c = 19{\cdot}812$ (7) Å, $U = 3583$ (1) Å^3, $Z = 2$, $D_x = 1{\cdot}651$, $D_m = 1{\cdot}643$ g cm^{-3}, μ(Mo $K\alpha$) = 13·3 cm^{-1}, $T = 295$ K, λ(Mo $K\alpha$) = 0·71069 Å, $F(000) = 1800$. $R = 0{\cdot}037$ for 1905 observed reflections with $I > 2{\cdot}5\sigma(I)$. The structure was solved by standard Patterson and Fourier techniques. It contains linear 4-ethyl-1,2,4-triazole (Ettrz) bridged trinuclear cations. The central Zn is octahedrally coordinated by six N atoms and the terminal Zn atom by three N atoms and three O atoms of water molecules.

Introduction. The present communication concerns an investigation that is part of a research project on the coordination chemistry of 4-substituted 1,2,4-triazoles (Vos, Haasnoot & Groeneveld, 1981; Vos, de Kok & Verschoor, 1981; Groeneveld, Vos, Verschoor & Reedijk, 1982; Vos, 1983). The 4-*R*-1,2,4-triazole ligand is found to coordinate either with one N atom or with two N atoms as a bridging ligand. This last coordination mode makes these ligands very interesting, especially from a magnetochemistry point of view, since through these bridging ligands, metal ions can be coupled magnetically. With transition-metal(II) thiocyanates, 4-*R*-1,2,4-triazoles (*R* = ethyl, allyl or *tert*-butyl) mainly give rise to the formation of dinuclear compounds (Vos, de Kok & Verschoor, 1981; Vos, Haasnoot & Groeneveld, 1981; Vos, 1983). With

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4-*tert*-butyl-1,2,4-triazole a number of linear trinuclear compounds were obtained as well (Groeneveld, Vos, le Fêbre, de Graaff & Haasnoot, 1983). The terminal coordination sites in these compounds are occupied by anions, water molecules or triazole ligands that coordinate by one N atom only.

Attempts to synthesize linear-chain compounds with Ettrz ligands in conjunction with the non-coordinating $CF_3SO_3^-$ anion resulted in a series of isomorphous compounds of composition $[M_3\ (\mathrm{Ettrz})_6(H_2O)_6](CF_3SO_3)_6$, with $M = \mathrm{Mn^{II}}, \mathrm{Fe^{II}}, \mathrm{Co^{II}}, \mathrm{Ni^{II}}, \mathrm{Zn^{II}}$ (Vos, 1983). The cations appear to be isostructural with the trinuclear cations reported by Reimann & Zocchi (1971) for the corresponding triazole compound in the presence of the non-coordinating nitrate anion.

The $\mathrm{Fe^{II}}$ compound exhibits a high-spin low-spin transition of the central metal ion upon cooling. An investigation by magnetic susceptibility, Mössbauer and X-ray diffraction techniques has been reported by Vos, le Fêbre, de Graaff, Haasnoot & Reedijk (1983).

Experimental. Transparent colourless crystal, 0·4 × 0·5 × 0·6 mm, mounted inside a Lindemann-glass capillary. Enraf–Nonius CAD-4F diffractometer (Zr-filtered Mo $K\alpha$); unit-cell dimensions from the setting angles of 24 carefully centred reflections. The metrical values indicated trigonal lattice symmetry. The correct Laue symmetry was ascertained as $\bar{3}1m$ *via* a study of the reflection symmetry within a shell of a sphere of reflections bounded by $\theta = 10$ and 15°. A set of 4121 reflections were averaged into 381 unique reflections with an averaging index of 0·047. The quality and absorption effects of the crystal were studied with ω and ψ scans and considered to be acceptable and negligible respectively. Observed systematic extinctions hhl: $l = 2n + 1$ indicated space groups $P31c$ and $P\bar{3}1c$. A one-quarter sphere of reflections $(h,k,\pm l)$ was collected ($\theta_{\max} = 27{\cdot}5°$; $\omega/2\theta$ scan mode) and averaged into a unique set of 2754 reflections. Lorentz–polarization corrections and corrections for the long and short-term instabilities as monitored by three reference reflections (224; $\bar{4}24$; $2\bar{4}4$; no indication of decay during data collection). Short-term corrections did not exceed 2%. 1905 reflections with $I > 2{\cdot}5\sigma(I)$ were used in the subsequent structure determination and refinement. Experimental density determined with the neutral buoyancy method in cyclohexane–1,2-dibromoethane.

Structure determination: standard Patterson and Fourier techniques, full-matrix least-squares refinement [minimizing $\sum w(\Delta F)^2$]. The $CF_3SO_3^-$ anion showed disorder, which was analysed as shown in Fig. 1 in terms of two alternative positions with a refined occupation ratio of 0·87:0·13, with the two pivot atoms S(1) and O(1) in common. Potential refinement instabilities due to overlap of the electron densities could be successfully controlled *via* slack constraints on the equivalent S=O, C—F and S—C bond lengths. The two H atoms of the water molecule were located in a difference Fourier map and their positional parameters refined. The remaining H atoms were introduced at calculated positions and refined in the riding mode on their carrier atoms. All positional and anisotropic thermal parameters of the non-hydrogen atoms were refined except for those of the minor fraction of the disordered anion atoms that were refined with one overall isotropic parameter. One overall parameter was used for the temperature factor of the H atoms. Final $R = 0{\cdot}037$ $\{R_w = 0{\cdot}041;$ $w^{-1} = [\sigma^2(F) + 0{\cdot}001F^2]/1{\cdot}94;$ $S = 1{\cdot}37;$ 184 parameters$\}$. Final difference Fourier map showed no significant residual features other than in the immediate region of the Zn atoms (attributable to absorption). Neutral scattering factors from Cromer & Mann (1968), corrected for anomalous-dispersion effects (Cromer & Liberman, 1970). In-house ECLIPSE S/230 minicomputer using the programs of the *ILIAS* package [an adaptation and extension (by ALS) of the *SHELX*76 package (Sheldrick, 1976)], or CDC-CYBER175 of the University of Utrecht with programs of the *EUCLID* package [calculation of geometrical data and preparation of illustrations including an extended version of the program *PLUTO* (Spek, 1982)].

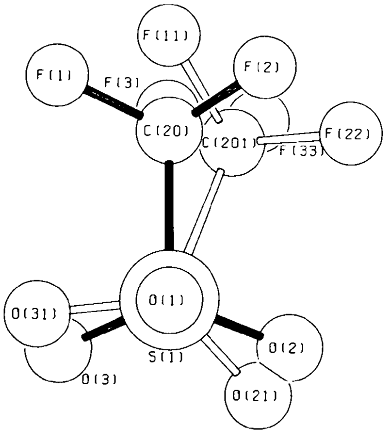

Fig. 1. Disorder model for the $CF_3SO_3^-$ anion in terms of an 87:13 statistical occupation ratio over two sites.

Discussion. Atomic coordinates are given in Table 1,* relevant data on the geometry in Table 2. The unit cell contains two formula units as depicted in Fig. 2. The cations are located in the cell on positions with site symmetry 32. The packing consists essentially of the alternate stacking of layers of anions at $z = 0$ and $\frac{1}{2}$ and cations at $z = \frac{1}{4}$ and $\frac{3}{4}$. The water molecules in the structure both coordinate to the Zn atoms and donate their H atoms to O atoms of the $CF_3SO_3^-$ anions as

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* A list of structure factors, all refined parameters (including anisotropic thermal parameters and H atom and disordered $CF_3SO_3^-$ coordinates) and additional data on the geometry have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 38506 (17 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Table 1. *Final coordinates and equivalent isotropic thermal parameters* (Å^2)

$$U_{eq} = \tfrac{1}{3}\textstyle\sum_i\sum_j U_{ij} a^*_i a^*_j \mathbf{a}_i.\mathbf{a}_j.$$

	x	y	z	U_{eq}
Zn(1)	0·3333	0·6667	0·25	0·0230 (2)
Zn(2)	0·3333	0·6667	0·05746 (2)	0·0274 (1)
S(1)	0·64560 (9)	0·66491 (9)	−0·09137 (4)	0·0518 (3)
F(1)	0·7825 (5)	0·8203 (5)	−0·1645 (4)	0·164 (3)
F(2)	0·8113 (5)	0·8442 (8)	−0·0587 (7)	0·193 (6)
F(3)	0·8460 (4)	0·7364 (5)	−0·1126 (5)	0·186 (4)
O(1)	0·5859 (3)	0·7180 (3)	−0·0856 (2)	0·082 (1)
O(2)	0·6525 (5)	0·6187 (4)	−0·0289 (2)	0·084 (2)
O(3)	0·6271 (5)	0·5961 (4)	−0·1475 (2)	0·103 (2)
O(4)	0·2261 (2)	0·6793 (2)	−0·0098 (1)	0·0419 (8)
N(1)	0·4513 (2)	0·6585 (2)	0·1173 (1)	0·0303 (7)
N(2)	0·4549 (2)	0·6651 (2)	0·1869 (1)	0·0292 (6)
N(3)	0·5896 (2)	0·6507 (2)	0·1522 (1)	0·0395 (8)
C(1)	0·5379 (2)	0·6600 (2)	0·2058 (1)	0·0361 (8)
C(2)	0·5333 (2)	0·6504 (2)	0·0984 (1)	0·0374 (9)
C(3)	0·6865 (3)	0·6399 (4)	0·1525 (2)	0·061 (1)
C(4)	0·6643 (4)	0·5390 (6)	0·1847 (3)	0·097 (3)
C(20)	0·7782 (7)	0·772 (1)	−0·1052 (7)	0·103 (4)

Table 2. *Relevant data on the geometry of* $[Zn_3(Ettrz)_6(H_2O)_6](CF_3SO_3)_6$

(i) Bond distances (Å)

Zn(1)–N(2)	2·165 (2)	F(3)–C(20)	1·32 (1)
Zn(2)–N(1)	2·127 (2)	N(1)–N(2)	1·382 (3)
Zn(2)–O(4)	2·120 (2)	N(1)–C(2)	1·302 (4)
S(1)–O(3)	1·424 (5)	N(2)–C(1)	1·293 (4)
S(1)–O(1)	1·416 (4)	N(3)–C(1)	1·345 (4)
S(1)–O(2)	1·433 (5)	N(3)–C(3)	1·484 (5)
S(1)–C(20)	1·78 (1)	N(3)–C(2)	1·340 (4)
F(1)–C(20)	1·35 (2)	C(3)–C(4)	1·47 (1)
F(2)–C(20)	1·29 (2)		

(ii) Bond angles (°)

N(2)–Zn(1)–N(2*a*)	90·0 (1)	Zn(1)–N(2)–N(1)	125·0 (2)
N(2)–Zn(1)–N(2*c*)	89·3 (1)	Zn(1)–N(2)–C(1)	127·8 (2)
N(2)–Zn(1)–N(2*d*)	90·7 (1)	N(1)–N(2)–C(1)	106·8 (2)
N(2)–Zn(1)–N(2*e*)	179·0 (1)	N(2)–C(1)–N(3)	110·8 (2)
N(1)–Zn(2)–N(1*a*)	92·0 (1)	N(1)–C(2)–N(3)	110·5 (3)
N(1)–Zn(2)–O(4)	174·6 (1)	C(1)–N(3)–C(2)	105·1 (3)
N(1)–Zn(2)–O(4*a*)	92·8 (1)	C(1)–N(3)–C(3)	127·5 (3)
N(1)–Zn(2)–O(4*b*)	90·3 (1)	C(2)–N(3)–C(3)	127·4 (3)
O(4)–Zn(2)–O(4*a*)	84·7 (1)	N(3)–C(3)–C(4)	110·8 (4)
Zn(2)–N(1)–N(2)	123·8 (2)	N(2)–N(1)–C(2)	106·7 (2)
Zn(2)–N(1)–C(2)	129·5 (2)		

(iii) Torsion angles (°)

Zn(1)–N(2)–N(1)–Zn(2)	7·4 (3)	Zn(2)–N(1)–C(2)–N(3)	178·3 (2)
Zn(1)–N(2)–C(1)–N(3)	174·2 (2)	C(1)–N(3)–C(3)–C(4)	64·8 (6)

(iv) Least-squares plane (in terms of fractional coordinates x,y,z) determined by the starred atoms, and distances of atoms from this plane (Å)

$$0{\cdot}97\,(2)x + 11{\cdot}98\,(1)y - 1{\cdot}14\,(4)z - 8{\cdot}195\,(7) = 0$$

N(1)* −0·002 (13); N(2)* 0·001 (14); N(3)* −0·001 (15); C(1)* 0·000 (15); C(2)* 0·002 (14); Zn(1) −0·170 (15); Zn(2) 0·049 (12); C(3) −0·036 (16); C(4) −1·303 (17).

Symmetry codes: (*a*) $1-y,\ 1+x-y,\ z$; (*b*) $y-x,\ 1-x,\ z$; (*c*) $1-y,\ 1-x,\ \tfrac{1}{2}-z$; (*d*) $x,\ 1+x-y,\ \tfrac{1}{2}-z$; (*e*) $y-x,\ y,\ \tfrac{1}{2}-z$.

shown in Fig. 3 [O(4)···O(1) $(1-y, 1+x-y, z)$ = 2·853 (6); O(4)···O(2) $(x-y, x, -z)$ = 2·718 (9) Å].

The linear trinuclear cations are similar to those reported by Reimann & Zocchi (1971) for $[Ni_3(trz)_6(H_2O)_6](NO_3)_6.2H_2O$. The bond lengths and angles of the 1,2,4-triazole moieties are essentially the same. The Zn(1)–Zn(2) distance is 3·815 (1) Å. This is significantly smaller than the corresponding Mn(1)–Mn(2) = 3·950 (2) Å distance in the isomorphous Mn compound (Vos, 1983).

The authors thank Dr A. J. M. Duisenberg for the data collection and Professor J. Reedijk for his interest in this study. The investigations were supported in part by the Netherlands Foundation for Chemical Research (SON) with financial aid from the Netherlands Organization for Advancement of Pure Research (ZWO).

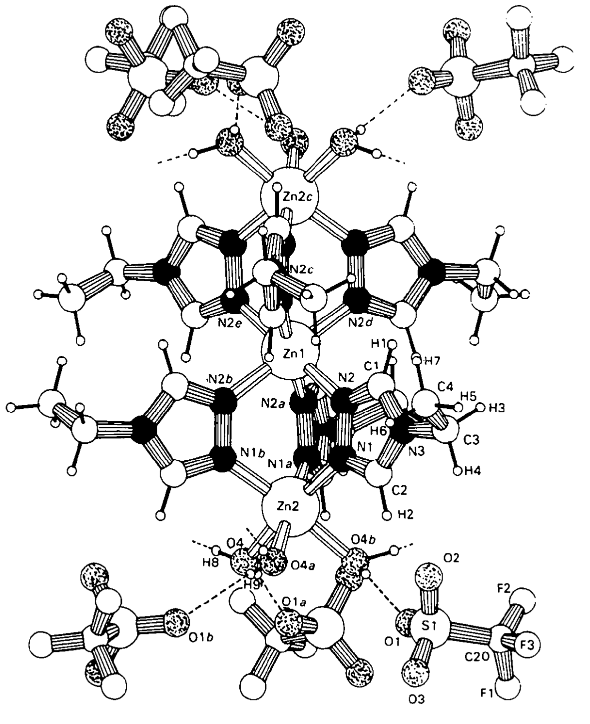

Fig. 2. A drawing of $[Zn_3(Ettrz)_6(H_2O)_6](CF_3SO_3)_6$. Hydrogen bonds are indicated by dashed lines.

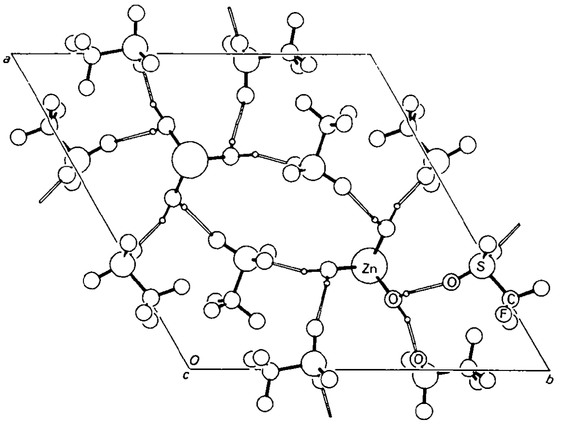

Fig. 3. Projection down the c axis of the hydrogen-bond network in $[Zn_3(Ettrz)_6(H_2O)_6](CF_3SO_3)_6$ within the anionic layer near $z = 0$.

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Acta Cryst. (1983). C**39**, 993–994

{2,4-Bis[1,1-dimethyl-2-(methylthio)ethyl]-3-furyl-*S*,*S*}chloropalladium(II), $[Pd(C_{14}H_{23}OS_2)Cl]$

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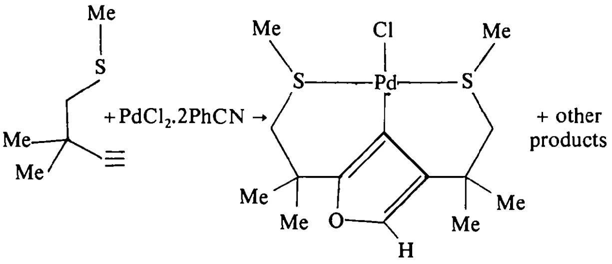
(*Received* 15 *February* 1983; *accepted* 12 *April* 1983)

Abstract. $M_r = 413\cdot3$, monoclinic, $P2_1/n$, $a = 10\cdot332\,(3)$, $b = 9\cdot957\,(2)$, $c = 16\cdot189\,(5)$ Å, $\beta = 103\cdot16\,(2)°$, $V = 1621\cdot7$ Å^3, $Z = 4$, $D_x = 1\cdot69$ g cm^{-3}, $F(000) = 840$, $T = 293$ K, μ(Mo $K\alpha$) = 15·3 cm^{-1}, $\lambda = 0\cdot71069$ Å, $R = 0\cdot018$ for 2589 observed data. The Pd atom is four coordinate in a close to square-planar environment, with Pd—Cl 2·388 (1), Pd—S 2·299 (1) and 2·307 (1), and Pd—C 2·007 (2) Å. The two six-membered rings adopt different conformations, one a twist-boat and the other a twist-chair.

Introduction. The reaction of 2,2-dimethyl-3-butynyl methyl sulphide (1) with dichlorobis(benzonitrile)palladium results in a novel product, (2) (the title compound) along with four other products (McCrindle, Ferguson, Arsenault, McAlees & Parvez, 1983). The structure of (2) was determined by our X-ray analysis which shows it to be an entirely new type of product obtained from the oligomerization of the acetylene (1).



(1) (2)

Experimental. Yellow crystals from dichloromethane, 0·25 × 0·22 × 0·20 mm, CAD-4 diffractometer, graphite-monochromatized Mo $K\alpha$ radiation, 25 reflections with θ in the range $10 < \theta < 15°$ used for measuring lattice constants; for data collection $2 < \theta < 25°$ (h −12–11, k 0–11, l 1–19), ω–2θ scans, ω-scan width $(0\cdot80 + 0\cdot35\tan\theta)°$; intensities of three reflections monitored every 3 h of exposure time showed no significant variation; Lp corrections, 2853 unique reflections, 2589 (90·7%) with $I > 3\sigma(I)$, where $\sigma^2(I) = S + 2B + [0\cdot04(S-B)]^2$, S = scan count and B = time-averaged background count; absorption correction was not considered necessary. Heavy-atom method using the *NRC Crystal Structure Package* (Larson & Gabe, 1978), refinement by block-diagonal least-squares calculations on F, H atoms from difference syntheses included at their idealized positions (C—H 0·95 Å) but not refined. Final $R = 0\cdot018$, $R_\omega = 0\cdot021$ for 2589 observed data, $R = 0\cdot021$ for all data, $\omega = 1/\sigma^2(F)$, GOF = 3·17, $\Delta\rho = \pm 0\cdot1$ e Å^{-3} in final difference map, maximum shift/e.s.d. = −0·30 for U_{23} of C(12), mean shift/e.s.d. = 0·07; atomic scattering factors from Cromer & Mann (1968) and Stewart, Davidson & Simpson (1965). Other computer programs used included *XANADU* (Roberts & Sheldrick, 1975) and *ORTEP* II (Johnson, 1976). Final fractional coordinates with mean isotropic temperature factors are in Table 1. Table 2 contains molecular dimensions.*

Discussion. The crystal structure contains discrete monomeric molecules (Fig. 1) separated by normal van der Waals distances. The Pd atom is four-coordinate in a close to square-planar environment; deviations of the

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* Lists of structure factors, anisotropic thermal parameters and the calculated hydrogen coordinates, as well as ring torsion angles, have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 38524 (24 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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