

[Cr(CO)₅(C₂H₄)] and has shown that, thanks to the equivalence of the two *d* orbitals with which the π^* molecular orbital can interact, there can be no electronic preference for any particular orientation of the ethene molecule (Albright, Hoffmann, Thibeault & Thorn, 1979). In [Ru(CO)(COPh)Ph(CNCMe₃)(PMe₂Ph)₂], however, the two *d* orbitals with which the π system of the phenyl ligand can interact are *not* equivalent: one must be shared with carbonyl, acyl and isocyanide ligands and the other with carbonyl and PMe₂Ph ligands. The orientation adopted by the phenyl ring allows maximum overlap with the *latter d* orbital, as would be expected since PMe₂Ph is a relatively poor π acceptor.

Delocalization between the carbonyl group and the phenyl ring within the benzoyl ligand must be severely inhibited by the non-planar geometry of this ligand, which may be the result of steric effects. It is noticeable that the Ru—C bond to the benzoyl ligand [2.142 (15) Å] is shorter than that to the phenyl ligand

[2.187 (12) Å]. This may result from the difference in π -acceptor strength between isocyanide (*trans* to benzoyl) and carbonyl (*trans* to phenyl) ligands.

We thank the SERC for maintenance grants (to DRS and MS).

References

- ALBRIGHT, T. A., HOFFMANN, R., THIBEAULT, J. C. & THORN, D. L. (1979). *J. Am. Chem. Soc.* **101**, 3801–3812.
 ASHWORTH, T. V., NOLTE, M. J., SINGLETON, E. & LAING, M. (1977). *J. Chem. Soc. Dalton Trans.* pp. 1816–1822.
 BARNARD, C. F. J., DANIELS, J. A. & MAWBY, R. J. (1976). *J. Chem. Soc. Dalton Trans.* pp. 961–966.
 BARNARD, C. F. J., DANIELS, J. A. & MAWBY, R. J. (1979). *J. Chem. Soc. Dalton Trans.* pp. 1331–1338.
International Tables for X-ray Crystallography (1974). Vol. IV, Tables 2.2.B and 2.3.1. Birmingham: Kynoch Press.
 KOMIYA, S., ITO, T., COWIE, M., YAMAMOTO, A. & IBERS, J. A. (1976). *J. Am. Chem. Soc.* **98**, 3874–3884.
 SHELDRIK, G. M. (1976). *SHELX76*. Program for crystal structure determination, Univ. of Cambridge, England.

Acta Cryst. (1983). **C39**, 987–990

Trilithium Citrate Pentahydrate, C₆H₅O₇³⁻·3Li⁺·5H₂O

BY MIRIAM ROSSI,* LORI F. RICKLES AND JENNY P. GLUSKER

Institute for Cancer Research, Fox Chase Cancer Center, 7701 Burholme Avenue, Philadelphia, Pennsylvania 19111, USA

(Received 17 January 1983; accepted 24 March 1983)

Abstract. $M_r = 299.92$, monoclinic, $A2/a$, $a = 12.216$ (1), $b = 19.972$ (1), $c = 10.725$ (1) Å, $\beta = 101.52$ (8)°, $V = 2563.9$ (4) Å³, $Z = 8$, $D_x = 1.554$ g cm⁻³, $Cu K\alpha$, $\lambda = 1.5418$ Å, $\mu = 13.27$ cm⁻¹, $F(000) = 1248$, room temperature. The crystal structure was solved by direct methods and refined by full-matrix least-squares techniques (non-hydrogen atoms anisotropic, H atoms isotropic) to a final $R = 0.034$ for 2244 independent observed reflections. The hydrogen bonding and the charge distribution are discussed.

Introduction. Two types of colorless crystals were obtained by evaporating an aqueous ethanolic solution of anhydrous trilithium citrate (Sigma Chemical Co.). One type, which crystallized first, appeared as plates, but these proved not to be single. The second type did not have a well defined morphology but diffracted well and therefore were used.

Experimental. Nicolet $P2_1$ diffractometer. Space group $A2/a$ from systematic absences (hkl , $k + l = 2n + 1$; $h0l$, $h = 2n + 1$; $0k0$, $k = 2n + 1$). Unit cell: 14 centered reflections, least-squares fit. Three-dimensional X-ray intensity data collected with θ - 2θ scan technique and graphite-monochromated $Cu K\alpha$ radiation. 2522 reflections scanned in the range $(\sin\theta)/\lambda = 0.05$ to 0.61 Å⁻¹ ($2\theta = 138^\circ$); 2355 had intensity (I) greater than the threshold of $2.0\sigma(I)$ [with $\sigma(I)$ derived from counting statistics]; of these, 2244 were unique and used in the structure solution and refinement. $\sigma(F) = (F/2)\{[\sigma^2(I)/I^2] + \delta^2\}^{1/2}$, where δ is the instrumental uncertainty ($\delta = 0.023$) determined from the variation in measured intensities in the periodically scanned standard reflections. The 2244 reflections and their associated standard deviations were converted to structure amplitudes by application of Lorentz and polarization factors and placed on an absolute scale with a Wilson plot; no absorption correction.

Structural solution obtained from *MULTAN* (Germain, Main & Woolfson, 1971) by use of 200 E values greater than 1.5. The solution with the highest absolute figure of merit (2.94) and lowest residual

* Present address: Chemistry Department, Vassar College, Poughkeepsie, NY 12601, USA.

(24.69%) gave an E map which revealed the positions of all the heavy atoms except for two of the Li^+ ions and the water molecules; the two Li^+ ions were found from a resulting electron density map. Two Li^+ were located in general positions and two were found to occupy special positions at $(\frac{1}{4}, y, 0)$ and $(\frac{1}{4}, y, \frac{1}{2})$. The solvent molecules were located in an electron density map calculated after a few cycles of isotropic refinement for the already determined atoms. Anisotropic refinement reduced the R value to 0.064 and all H atoms, including those on the solvent water molecules, were then located from the resulting difference electron density map. Their inclusion and subsequent refinement led to final residuals $R = 0.034$, and $wR = 0.049$. Largest ratio of shift to e.s.d. 0.7; $\sum w\Delta F^2$ minimized in the least-squares calculations; $w = 1/[\sigma^2(F)]$, with zero weight for the reflections below the threshold value; final difference electron density map showed the largest positive and negative peaks to be 0.35 and $-0.40 \text{ e } \text{Å}^{-3}$ respectively.

Computer programs used were a locally modified version of *UCLALS4* (Carrell, 1975; Gantzel, Sparks, Long & Trueblood, 1969) and other programs written in the Institute for Cancer Research laboratory. The atomic scattering factors used are from a compilation of published values (*International Tables for X-ray Crystallography*, 1974); those for H atoms were from Stewart, Davidson & Simpson (1965).

Discussion. Final refined coordinates and average equivalent isotropic temperature factors are listed in Table 1.* The numbering of atoms is shown in Fig. 1. Bond distances and interbond angles, shown in deposited figures and tables,* are those expected for triionized citrates (Glusker, 1980). The central α -hydroxycarboxylate grouping is approximately planar [torsion angle $-19.2(2)^\circ$ for $\text{O}(7)-\text{C}(3)-\text{C}(6)-\text{O}(5)$] and the anion contains an internal hydrogen bond between the hydroxyl H atom and a terminal carboxylate group. In order to form this hydrogen bond the backbone is not fully extended; the hydrogen-bonded carboxymethyl is rotated to give a $\text{C}(2)-\text{C}(3)-\text{C}(4)-\text{C}(5)$ torsion angle of $64.8(2)^\circ$. This is illustrated in Fig. 2.

The surroundings and geometry of each Li^+ ion are illustrated in Fig. 2. There are four types of Li^+ ions since $\text{Li}(2)$ and $\text{Li}(3)$ lie at $x = \frac{1}{4}$, $z = 0$ and $z = \frac{1}{2}$ respectively, with 50% occupancy per asymmetric unit. The coordinations of O atoms around the Li^+ ions are four for $\text{Li}(1)$, $\text{Li}(3)$ and $\text{Li}(4)$ and six for $\text{Li}(2)$. $\text{Li}-\text{O}$ distances range from 1.883(2) to 2.222(3) Å with the longest distances observed in the case of octahedral

coordination to $\text{Li}(2)$. A table of the coordination geometry around each Li cation has been deposited.* This is in line with data on two other lithium citrates – lithium dihydrogen citrate (Glusker, van der Helm, Love, Dornberg, Minkin, Johnson & Patterson, 1965) with an Li coordination number of 6 and lithium ammonium hydrogen citrate (Gabe, Glusker, Minkin & Patterson, 1967) with an Li coordination number of 4.

* See deposition footnote.

Table 1. Refined atomic parameters of trilithium citrate pentahydrate

Positional parameters are listed as fractions of cell edges. Isotropic temperature factors are listed as $\exp(-B\sin^2\theta/\lambda^2)$ with B values given in Å^2 . Estimated standard deviations with respect to the last digit listed are given in parentheses.

	x	y	z	$\langle B \rangle$
O(1)	0.5353 (1)	-0.12077 (4)	0.2576 (1)	2.12 (3)
O(2)	0.6412 (1)	-0.06774 (5)	0.4186 (1)	2.36 (3)
O(3)	0.4242 (1)	0.08487 (4)	0.0290 (1)	2.45 (3)
O(4)	0.3884 (1)	0.16633 (4)	0.1541 (1)	2.57 (3)
O(5)	0.2370 (1)	-0.09665 (5)	0.1820 (1)	2.29 (3)
O(6)	0.3018 (1)	-0.05731 (4)	0.3772 (1)	2.37 (3)
O(7)	0.3870 (1)	-0.03810 (4)	0.0826 (1)	1.54 (3)
C(1)	0.5616 (1)	-0.0697 (1)	0.3256 (1)	1.69 (4)
C(2)	0.4934 (1)	-0.0058 (1)	0.2935 (1)	1.81 (4)
C(3)	0.3784 (1)	-0.0126 (1)	0.2058 (1)	1.42 (4)
C(4)	0.3212 (1)	0.0567 (1)	0.1884 (1)	1.67 (4)
C(5)	0.3823 (1)	0.1068 (1)	0.1197 (1)	1.64 (4)
C(6)	0.2997 (1)	-0.0600 (1)	0.2602 (1)	1.59 (4)
Li(1)	0.4827 (2)	-0.1165 (1)	0.0784 (2)	1.95 (8)
Li(2)	0.2500	-0.1060 (2)	0.0000	1.28 (7)
Li(3)	0.2500	0.0012 (2)	0.5000	1.42 (6)
Li(4)	0.3226 (2)	0.2156 (1)	0.2709 (2)	2.32 (8)
O(W1)	0.6200 (1)	-0.18391 (5)	0.5558 (1)	2.82 (4)
O(W2)	0.1151 (1)	-0.19679 (5)	0.2464 (1)	2.58 (3)
O(W3)	0.3752 (1)	-0.18708 (4)	0.0528 (1)	2.36 (3)
O(W4)	0.6626 (1)	-0.23259 (5)	0.2402 (1)	2.70 (4)
O(W5)	0.3877 (1)	-0.1839 (1)	0.4822 (1)	3.51 (4)
H(7)	0.408 (1)	-0.004 (1)	0.042 (2)	3.1 (4)
H(20)	0.484 (1)	0.015 (1)	0.370 (2)	2.6 (3)
H(21)	0.541 (1)	0.027 (1)	0.257 (2)	2.4 (3)
H(40)	0.318 (1)	0.074 (1)	0.264 (2)	2.1 (3)
H(41)	0.248 (1)	0.055 (1)	0.142 (2)	2.4 (3)
H(10W1)	0.641 (2)	-0.152 (1)	0.523 (2)	4.5 (5)
H(20W1)	0.549 (2)	-0.182 (1)	0.538 (2)	5.0 (5)
H(10W2)	0.145 (2)	-0.164 (1)	0.233 (2)	4.3 (5)
H(20W2)	0.047 (2)	-0.188 (1)	0.215 (2)	4.4 (5)
H(10W3)	0.386 (2)	-0.219 (2)	0.027 (2)	6.5 (7)
H(20W3)	0.377 (2)	-0.204 (1)	0.135 (2)	5.3 (5)
H(10W4)	0.615 (2)	-0.195 (2)	0.236 (3)	8.1 (7)
H(20W4)	0.639 (2)	-0.249 (1)	0.166 (2)	4.7 (5)
H(10W5)	0.378 (2)	-0.191 (1)	0.560 (2)	5.7 (6)
H(20W5)	0.376 (2)	-0.136 (1)	0.465 (3)	7.1 (7)

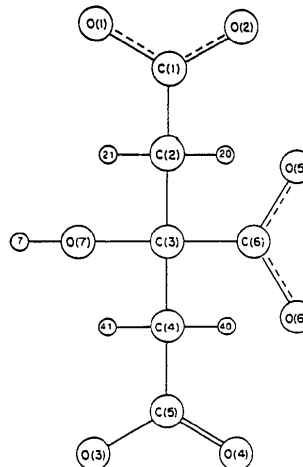


Fig. 1. Numbering of atoms.

* Lists of structure factors, anisotropic thermal parameters, interatomic distances and angles and a figure showing the unit-cell contents have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 38478 (21 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

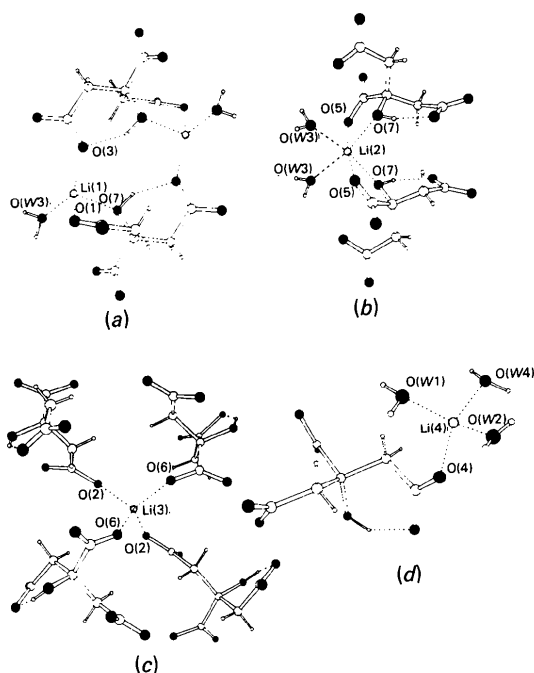


Fig. 2. Surroundings of Li^+ ions. (a) Li(1); (b) Li(2); (c) Li(3) and (d) Li(4). [This figure was produced by the computer program VIEW (Carrell, 1977).]

Table 2. Hydrogen bonds

$D-H\cdots A$	$D\cdots A$ (Å)	$D-H$ (Å)	$H\cdots A$ (Å)	$D-H\cdots A$ (°)
$O(7)-H(7)\cdots O(3)$	2.583 (1)	0.87 (2)	1.79 (2)	150 (2)
$O(W1)-H(10W1)\cdots O(2)$	2.787 (2)	0.79 (2)	2.03 (2)	162 (2)
$O(W1)-H(20W1)\cdots O(W5)$	2.789 (1)	0.85 (2)	1.95 (2)	174 (2)
$O(W2)-H(10W2)\cdots O(5)$	2.666 (1)	0.78 (2)	1.90 (2)	168 (2)
$O(W2)-H(20W2)\cdots O(4)$	2.815 (1)	0.86 (2)	1.96 (2)	176 (2)
$O(W3)-H(10W3)\cdots O(W1^{II})$	2.833 (2)	0.72 (3)	2.13 (3)	167 (2)
$O(W3)-H(20W3)\cdots O(W4^{III})$	2.850 (2)	0.94 (2)	1.97 (2)	155 (2)
$O(W4)-H(10W4)\cdots O(1)$	2.749 (1)	0.95 (3)	1.81 (3)	170 (2)
$O(W4)-H(20W4)\cdots O(W5^{II})$	2.874 (2)	0.86 (2)	2.05 (2)	159 (5)
$O(W5)-H(10W5)\cdots O(W2^{IV})$	2.930 (2)	0.87 (2)	2.07 (3)	169 (2)
$O(W5)-H(20W5)\cdots O(6)$	2.879 (2)	0.98 (3)	1.96 (3)	156 (2)

Symmetry code: superscript: none x, y, z ; (i) $-1\frac{1}{2}+x, -y, z$; (ii) $1-x, -y-\frac{1}{2}, \frac{1}{2}-z$; (iii) $1-x, -1\frac{1}{2}-y, -\frac{1}{2}-z$; (iv) $\frac{1}{2}-x, y, 1-z$.

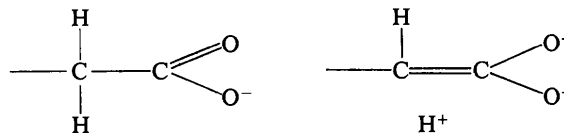
No similarity in the spatial arrangement of coordinated Li around citrate is discernible in these three forms of citrate.

The hydrogen-bonding scheme is listed in Table 2. Each water molecule donates two hydrogen bonds and is surrounded by two other groups, either an H atom donated from another water molecule or an Li^+ ion. Water molecule O(W5) is surrounded by four O atoms, water molecules O(W1), O(W2) and O(W4) by three O atoms and one Li^+ ion, and water molecule O(W3) by two O atoms and two Li^+ ions.

An analysis was made of the charge distribution using the equations of Brown (1981) following the earlier work of Pauling (1929), Donnay & Allmann (1970) and Brown & Shannon (1973). The equations used for charge were $s = (r/1.378)^{-4.065}$ for $\text{Li}^+\cdots\text{O}$ distances and $s = (r/0.87)^{-2.2}$ for $\text{H}^+\cdots\text{O}$ distances (in

hydrogen bonds), where s is the bond strength and r is the coordination distance. Ideally the values of s should total 1.0 around Li^+ and H^+ . The results, listed in Table 3, show more negative charge on the terminal than on the central carboxyl group. This may be related to the lengthening of the C(3)—C(6) bond, a feature of all citrates studied to date (Glusker, 1980); this lengthening is probably the result of the development of a slight positive charge on both C(3) and C(6), an effect related to the 'polymethine state' effect described by Kulpe & Dahne (1978).

Table 4 is a comparison of the structure determined here with those for lithium dihydrogen citrate (Glusker *et al.*, 1965), lithium ammonium hydrogen citrate (Gabe *et al.*, 1967) and lithium glycolate (Gabe & Taylor, 1966). Because the structure of lithium dihydrogen citrate was determined with projection data only, detailed use of results from that study cannot be made. Nevertheless, examination of the dimensions of lithium ammonium hydrogen citrate and trillithium citrate indicates that the C—C bond to the central carboxyl group is lengthened over that for the terminal $-\text{CH}_2-\text{COO}^-$ groups. This lengthening does not seem to occur in lithium glycolate and we conclude that the effect is the result of the presence of the $-\text{CH}_2-$ group adjacent to the carboxyl group which allows for resonance hybrids of the form



The second form is not possible for the central carboxyl group of citrate because there are no H atoms on the C atom adjacent to it. In addition the $O(5)\cdots O(7)$ distance in citrate is less than in glycolate because lengthening the C(3)—C(6) bond in the latter has not separated these O atoms. These conclusions suggest that the effect is electronic (hyperconjugative) rather than steric, resulting in more negative charge on the terminal carboxyl O atoms as seen in Table 3.

Table 3. Values of s computed for citrate and water O atoms

s is the bond strength and is computed (for coordination distance r) as $s = (r/1.378)^{-4.065}$ for $\text{Li}^+\cdots\text{O}$ distances and $s = (r/0.87)^{-2.2}$ for $\text{H}^+\cdots\text{O}$ distances (in hydrogen bonds). The total gives an indication of the charge on each O atom.

	Contributions				Hydrogen bonding	Total
	Li(1)	Li(2)	Li(3)	Li(4)		
O(1)	0.269				0.200	0.47
O(2)			0.240		0.155	0.40
O(3)	0.281				0.204	0.48
O(4)				0.274	0.167	0.44
O(5)		0.221			0.179	0.40
O(6)			0.239		0.167	0.41
O(7)	0.239	0.150			0.39	
O(W1)				0.240	0.137	0.38
O(W2)				0.254	0.146	0.40
O(W3)	0.266	0.143			0.166	0.41
O(W4)				0.246	0.166	0.41
O(W5)					0.169, 0.149	0.32

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.

References

- BROWN, I. D. (1981). *Structure and Bonding in Crystals*, Vol. II, pp. 1–30. New York, London: Academic Press.
- BROWN, I. D. & SHANNON, R. D. (1973). *Acta Cryst.* **A29**, 266–282.
- CARRELL, H. L. (1975). *ICRFMLS*. Modification of *UCLALS4*. Program from the Institute for Cancer Research, Philadelphia, PA.
- CARRELL, H. L. (1977). *VIEW: A Graphics Program for Molecular Diagrams*. Program from the Institute for Cancer Research, Philadelphia, PA.
- DONNAY, G. & ALLMANN, R. (1970). *Am. Mineral.* **55**, 1003–1015.
- GABE, E. J., GLUSKER, J. P., MINKIN, J. A. & PATTERSON, A. L. (1967). *Acta Cryst.* **22**, 366–375.
- GABE, E. J. & TAYLOR, M. R. (1966). *Acta Cryst.* **21**, 418–421.
- GANTZEL, P. K., SPARKS, R. A., LONG, R. E. & TRUEBLOOD, K. N. (1969). *UCLALS4*. A program in Fortran IV.
- GERMAIN, G., MAIN, P. & WOOLFSON, M. M. (1971). *Acta Cryst.* **A27**, 368–376.
- GLUSKER, J. P. (1980). *Acc. Chem. Res.* **13**, 345–352.
- GLUSKER, J. P., VAN DER HELM, D., LOVE, W. E., DORNBERG, M. L., MINKIN, J. A., JOHNSON, C. K. & PATTERSON, A. L. (1965). *Acta Cryst.* **19**, 561–572.
- International Tables for X-ray Crystallography* (1974). Vol. IV. Birmingham: Kynoch Press.
- KULPE, S. & DAHNE, S. (1978). *Acta Cryst.* **B34**, 3616–3623.
- PAULING, L. (1929). *J. Am. Chem. Soc.* **51**, 1010–1026.
- STEWART, R. F., DAVIDSON, E. R. & SIMPSON, W. T. (1965). *J. Chem. Phys.* **42**, 3175–3187.

Acta Cryst. (1983). **C39**, 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), [Zn₃(C₄H₇N₃)₆(H₂O)₆][CF₃SO₃]₆

BY A. L. SPEK

Laboratorium voor Structuurchemie, University of Utrecht, Padualaan 8, 3584 CH Utrecht, The Netherlands

AND G. VOS

Gorlaeus Laboratories, Section of Coordination Chemistry, Leiden State University, PO Box 9502, 2300 RA Leiden, The Netherlands

(Received 17 March 1983; accepted 4 April 1983)

Abstract. $M_r = 1781.32$, trigonal, $P\bar{3}1c$, $a = 14.450$ (2), $c = 19.812$ (7) Å, $U = 3583$ (1) Å³, $Z = 2$, $D_x = 1.651$, $D_m = 1.643$ g cm⁻³, $\mu(\text{Mo } K\alpha) = 13.3$ cm⁻¹, $T = 295$ K, $\lambda(\text{Mo } K\alpha) = 0.71069$ Å, $F(000) = 1800$. $R = 0.037$ for 1905 observed reflections with $I > 2.5\sigma(I)$. The structure was solved by standard Patterson and Fourier techniques. It contains linear 4-ethyl-1,2,4-triazole (Etrtz) 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 ($R = \text{ethyl, allyl or } tert\text{-butyl}$) mainly give rise to the formation of dinuclear compounds (Vos, de Kok & Verschoor, 1981; Vos, Haasnoot & Groeneveld, 1981; Vos, 1983). With