

- KLUG, H. P. (1968). *Acta Cryst.* B24, 792–802.
 KLUG, H. P. (1970). *Acta Cryst.* B26, 1268–1275.
 KUCSMAN, Á., KÁLMÁN, A. & KAPOVITS, I. (1967). *Acta Chim. Hung.* 53, 97–104.
 O'CONNOR, B. H. & MASLEN, E. N. (1965). *Acta Cryst.* 18, 363–366.
 PÁRKÁNYI, L., KÁLMÁN, A., ARGAY, GY. & SCHAWARTZ, J. (1977). *Acta Cryst.* B33, 3102–3106.
 POKRYWIECZKI, S., WEEKS, C. M. & DUAX, W. L. (1973a). *Cryst. Struct. Commun.* 2, 63–66.
 POKRYWIECZKI, S., WEEKS, C. M. & DUAX, W. L. (1973b). *Cryst. Struct. Commun.* 2, 67–72.
 PURNELL, L. G., SHEPHERD, J. C. & HODGSON, D. J. (1975). *J. Amer. Chem. Soc.* 97, 2376–2380.
 SCHOMAKER, V. & TRUEBLOOD, K. N. (1968). *Acta Cryst.* B24, 63–76.
 SHELDRIK, G. M. (1975). The *SHELX* crystal structure calculation program. Univ. of Cambridge, England.
 STADLER, D., AUSCHÜTZ, W., REGITZ, M., KELLER, G., VAN ASSCHE, D. & FLEURY, J.-P. (1975). *Liebigs. Ann.* pp. 2159–2168.
 STEWART, R. F., DAVIDSON, E. R. & SIMPSON, W. T. (1965). *J. Chem. Phys.* 42, 3175–3187.
 VORONTSOVA, L. G. (1966). *Zh. Strukt. Khim.* 7, 280–283.
 WHEATLEY, P. J. (1954). *Acta Cryst.* 7, 68–72.

Acta Cryst. (1977). B33, 3102–3106

The Crystal and Molecular Structure of 5-Amino-4-ethoxycarbonyl-1*H*-1,2,3-triazole, C₅H₈N₄O₂*

BY LÁSZLÓ PÁRKÁNYI, ALAJOS KÁLMÁN AND GYULA ARGAY

Central Research Institute for Chemistry, Hungarian Academy of Sciences, H-1525-Budapest, POB 17, Hungary

AND JÓZSEF SCHAWARTZ

Chinoin Works for Pharmaceutical and Chemical Products, H-1045-Budapest, IV Tó u. 5, Hungary

(Received 1 March 1977; accepted 2 April 1977)

C₅H₈N₄O₂ is monoclinic, space group $P2_1/c$, with $a = 10.667$ (2), $b = 6.287$ (2), $c = 10.881$ (2) Å, $\beta = 94.39$ (10)°, $Z = 4$. The structure was refined to $R = 0.085$ for 1281 observed reflexions. The tautomerism of the 1,2,3-triazoles can be characterized by the bond angles in the five-membered rings. The hydrogen bonding formed in the presence of the ethoxycarbonyl group is compared with that in related compounds.

Introduction

A minor by-product was isolated from the mother liquor of ethyl ethoxycarbonylacetimidate.HCl by ammonolysis (Pinner, 1895). It was identified as 1-ethoxycarbonylacetamidine.HCl (m.p. 110°C). This compound, like 1-carbamoylacetamidine, reacts with sulphonyl azide [Schawartz, Hornyák (née Hátori) & Szüts, 1970], and gives a sulphur-free colourless substance (m.p. 170°C). The X-ray analysis corroborated the predicted 1*H*-1,2,3-triazole structure.

Experimental

A crystal of 0.1 mm maximum dimension was mounted on a Syntex $P2_1$ computer-controlled four-circle diffractometer equipped with a graphite monochromator. Cell constants were determined by least squares from the setting angles of 15 reflexions.

* Dedicated to Professor A. Albert (Canberra) on his 70th birthday.

Crystal data

C₅H₈N₄O₂; $M_r = 156.1$, monoclinic; $a = 10.667$ (2), $b = 6.287$ (2), $c = 10.881$ (2) Å, $\beta = 94.39$ (10)°; $V = 727.58$ Å³; $D_c = 1.424$, $D_m = 1.42$ g cm⁻³, $Z = 4$. $F(000) = 328$, $\mu(\text{Mo } K\alpha, \lambda = 0.71069 \text{ Å}) = 0.74$ cm⁻¹, space group $P2_1/c$.

During data collection (Mo $K\alpha$ radiation) the intensities of 98 reflexions were lower than a preset limit and these were omitted from the measurement. 1301 reflexions were retained in the final set, 1281 of which had $|F| - 4.5\sigma(F) > 0$ and were taken as observed. No absorption correction was performed.

The structure was solved with *SHELX* (Sheldrick, 1975) from 246 normalized structure factors ($E \geq 1.20$) giving $R = 0.38$ for the non-hydrogen atoms. Prior to the refinement, all H atoms, except those linked to N atoms, were generated with a staggered methyl group assumed and with C–H constrained to 1.08 Å. Blocked full-matrix least-squares refinement for the non-hydrogen atoms gave a final R of 0.085 [$R_G = (\sum w\Delta^2 / \sum w|F_o|^2)^{1/2} = 0.099$] for the observed reflexions ($R_{\text{tot}} = 0.089$ for all 1301 reflexions). The weights

were given by $w = k/[\sigma^2(F_o) + gF_o^2]$ where k and g refined to 20.436 and 0.00036, respectively. A bonded-H-atom scattering factor was employed (Stewart, Davidson & Simpson, 1965) with complex neutral scattering factors for the remaining atoms (Cromer & Mann, 1968; Cromer & Liberman, 1970). The calculations were performed with *SHELX* (Sheldrick, 1975). The final coordinates for the non-hydrogen atoms are given in Table 1, the parameters for the H

Table 1. Fractional coordinates ($\times 10^4$)

Estimated standard deviations are given in parentheses.

| | <i>x</i> | <i>y</i> | <i>z</i> |
|------|----------|-----------|----------|
| O(1) | 7109 (3) | -1463 (4) | 6341 (3) |
| O(2) | 7183 (2) | 2008 (4) | 5847 (3) |
| N(1) | 9326 (3) | -2004 (4) | 3369 (3) |
| N(2) | 9374 (3) | 141 (5) | 3152 (2) |
| N(3) | 8720 (3) | 1077 (4) | 3968 (3) |
| N(4) | 8423 (4) | -4350 (5) | 4789 (3) |
| C(1) | 8253 (3) | -417 (5) | 4695 (3) |
| C(2) | 8638 (5) | -2413 (5) | 4327 (3) |
| C(3) | 7462 (3) | -40 (5) | 5704 (3) |
| C(4) | 6351 (4) | 2527 (7) | 6814 (4) |
| C(5) | 5025 (4) | 2264 (9) | 6354 (5) |

Table 2. Fractional coordinates ($\times 10^3$) [common thermal parameter $\bar{u} = 0.086$ (7) \AA^2] and bond distances (\AA) for the hydrogen atoms

| | <i>x</i> | <i>y</i> | <i>z</i> | <i>X-H</i> | <i>X</i> |
|-------|----------|----------|----------|------------|----------|
| H(1) | 982 | -269 | 291 | 0.87 | N(1) |
| H(41) | 797 | -442 | 537 | 0.82 | N(4) |
| H(42) | 856 | -538 | 457 | 0.71 | N(4) |
| H(4a) | 656 | 151 | 761 | 1.08 | C(4) |
| H(4b) | 659 | 416 | 707 | 1.08 | C(4) |
| H(5a) | 483 | 314 | 551 | 1.08 | C(5) |
| H(5b) | 438 | 275 | 702 | 1.08 | C(5) |
| H(5c) | 492 | 58 | 617 | 1.08 | C(5) |

Table 4. Rigid-body librational analysis

Centre which gives symmetric S: 0.8735, -0.0744, 0.4200.

| | <i>L</i> ($\text{rad}^2 \times 10^{-4}$) | <i>S</i> ($\text{rad} \text{\AA} \times 10^{-4}$) | <i>T</i> ($\text{\AA}^2 \times 10^{-4}$) |
|--|--|---|--|
| | 59 (7) | -19 (5) | -41 (6) |
| | | 26 (6) | 29 (5) |
| | | | 73 (7) |
| | 9 (8) | 2 (9) | 1 (7) |
| | 2 (6) | 10 (9) | 6 (8) |
| | 1 (7) | 6 (11) | -19 (9) |
| | 347 (19) | -21 (16) | 35 (17) |
| | | 225 (16) | -4 (15) |
| | | | 373 (18) |

atoms in Table 2 and the bond distances and angles in Table 3.†

An analysis of the thermal parameters of the non-hydrogen atoms was performed with rigid-body motion of the molecule assumed (Schomaker & Trueblood, 1968). The generalized $R_{UG} = [\sum (U_c - U_o)^2 / \sum U_o^2]^{1/2}$ was 0.100. The results are presented in Table 4 and have been used to apply the libration correction to the bond lengths (Table 3).

Discussion

The non-hydrogen atoms, except C(5) [$\Delta = -1.437 \text{\AA}$], are at an average distance of 0.22 \AA from the least-squares plane given by: $8.188x + 0.582y + 6.241z - 9.649 = 0$, where x, y, z are coordinates referred to orthogonal axes a^*, b, c . The triazole ring is planar; the maximum deviation from the best plane ($8.276x + 0.440y + 6.157z - 9.705 = 0$), obtained for the ring

† Lists of structure factors and anisotropic thermal parameters have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 32634 (10 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 13 White Friars, Chester CH1 1NZ, England.

Table 3. Interatomic distances (\AA) and bond angles ($^\circ$) with their *e.s.d.*'s in parentheses

Librationally corrected bond lengths are given in square brackets.

| | | | | | |
|----------------|-----------|---------|----------------|-----------|---------|
| O(1)-C(3) | 1.210 (4) | [1.218] | N(2)-N(3) | 1.310 (4) | [1.313] |
| O(2)-C(3) | 1.334 (4) | [1.341] | N(3)-C(1) | 1.384 (4) | [1.356] |
| O(2)-C(4) | 1.464 (5) | [1.467] | N(4)-C(2) | 1.344 (5) | [1.354] |
| N(1)-N(2) | 1.371 (4) | [1.380] | C(1)-C(2) | 1.389 (4) | [1.395] |
| N(1)-C(2) | 1.345 (5) | [1.350] | C(1)-C(3) | 1.454 (5) | [1.457] |
| | | | C(4)-C(5) | 1.474 (6) | [1.483] |
| C(4)-O(2)-C(3) | 116.9 (3) | | C(2)-C(1)-N(3) | 109.3 (3) | |
| C(2)-N(1)-N(2) | 110.5 (3) | | C(3)-C(1)-N(3) | 126.3 (3) | |
| N(3)-N(2)-N(1) | 107.3 (3) | | C(3)-C(1)-C(2) | 124.5 (3) | |
| C(1)-N(3)-N(2) | 108.9 (3) | | O(2)-C(3)-O(1) | 124.4 (3) | |
| N(4)-C(2)-N(1) | 125.6 (3) | | C(1)-C(3)-O(1) | 122.4 (3) | |
| C(1)-C(2)-N(1) | 104.0 (3) | | C(1)-C(3)-O(2) | 113.2 (3) | |
| C(1)-C(2)-N(4) | 130.4 (3) | | C(5)-C(4)-O(2) | 110.5 (4) | |

atoms, is 0.002 Å, in agreement with the strong multiple bonds within and between the ring and the substituents (Table 3). The endocyclic H atom, as expected, was found to be bound to N(1), and as in 5-amino-4-carbamoyl-1*H*-1,2,3-triazole (Kálmán, Si-

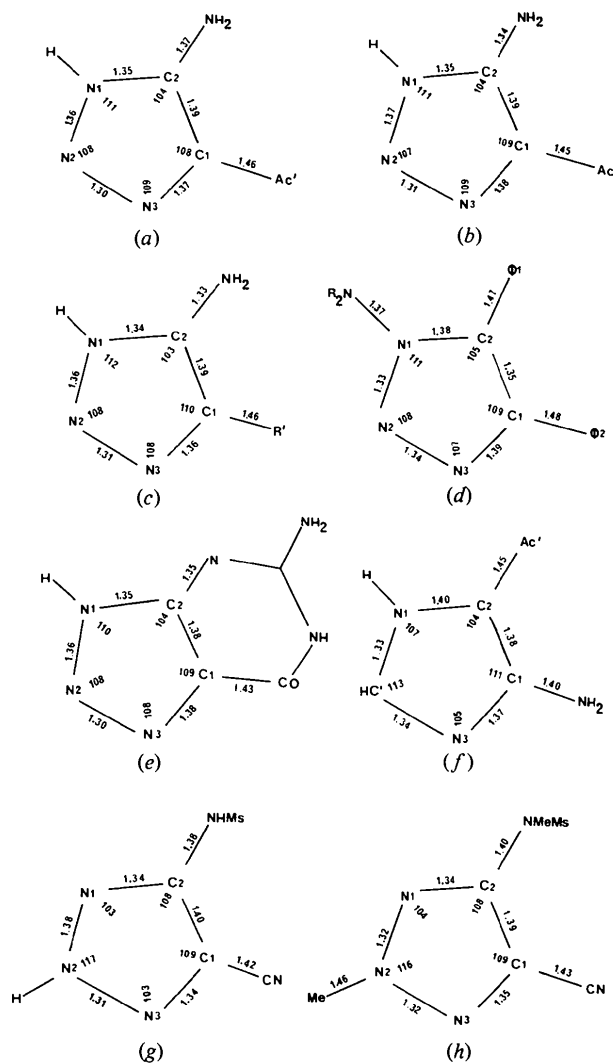


Fig. 1. Bond distances (Å) and angles (°) for 1,2,3-triazole rings with different substituents and environments including an imidazole derivative (*f*) analogous to (*a*) [N(2) is replaced by a CH group]. (*a*) 5-Amino-4-carbamoyl-1*H*-1,2,3-triazole (Kálmán, Simon, Schwartz & Horváth, 1974). (*b*) Present work. (*c*) Tetrachlorobis[2-(5-amino-4-carboxamidinium)-1*H*-1,2,3-triazole]copper(II) (Purnell, Shepherd & Hodgson, 1975). (*d*) 1-(α -*o*-Bromobenzoyloxy-*o*'-bromobenzylideneamino)-4,5-diphenyl-1,2,3-triazole (Kokkou & Rentzeperis, 1975). (*e*) 8-Azaguanidine (Sletten, Sletten & Jensen, 1968). (*f*) 4-Amino-5-carbamoyl-1*H*-imidazole monohydrate (Simon, Schwartz & Kálmán, 1977), (*g*) 5-Mesyamino-2*H*-1,2,3-triazole-4-carbonitrile monohydrate (Kálmán, Párkányi, Schwartz & Simon, 1976). (*h*) 2-Methyl-5-[methyl(mesy)amino]-2*H*-1,2,3-triazole-4-carbonitrile (Kálmán, Párkányi & Schwartz, 1977) (angle at N3: 103°).

mon, Schwartz & Horváth, 1974), tetrachlorobis[2-(5-amino-4-carboxamidinium)-1*H*-1,2,3-triazole]copper (II) (Purnell, Shepherd & Hodgson, 1975) and 8-azaguanidine (Sletten, Sletten & Jensen, 1968) is accompanied by a strong, almost double, bond between N(2) and N(3) (Fig. 1). This proof of the 1*H*-tautomeric form is weakened by the fact that a similar short N(2)—N(3) bond (1.310 Å) was also found in 5-mesyamino-2*H*-1,2,3-triazole-4-carbonitrile monohydrate (Kálmán, Párkányi, Schwartz & Simon, 1976). As seen in Fig. 1 the 1*H*- and 2*H*-structures can be distinguished, however, by analysis of the endocyclic bond angles. The 1*H*-tautomers have different angles at N(1), N(2), N(3) and C(2) from those in the 2*H*-structures (Table 5).

While the angles at the N atoms in 1*H*-triazoles differ only slightly from each other, they are definitely different from the corresponding angles of the 2*H*-structures. The analogous 4-amino-5-carbamoyl-1*H*-imidazole monohydrate (second column in Table 5) has bond angles intermediate between the corresponding 1*H*- and 2*H*-1,2,3-triazole values, but it can be distinguished from the triazoles on the basis of the four bond angles. The differences between the bond angles involving N atoms to which are bonded an endocyclic H and those of the bare N atoms have been discussed elsewhere (Kálmán *et al.*, 1976).

The analysis of 5-amino-4-carbamoyl-1*H*-1,2,3-triazole (Kálmán *et al.*, 1974) and the analogous 4-amino-5-carbamoyl-1*H*-imidazole monohydrate (Simon, Schwartz & Kálmán, 1977) revealed fairly complicated hydrogen-bond networks (Kálmán & Simon, 1975). Both structures are built up from dimers depicted in Fig. 2. Each corner of these dimers is either donor or acceptor in forming complicated hydrogen-bond networks. This ability of the title compound is considerably diminished by the replacement of the carbamoyl group by an ethoxycarbonyl moiety, as shown by the simple hydrogen-bond helices formed around screw axes (Fig. 3). These helices are independent of each other. In each helix there is only one strong hydrogen bond [N(1)—H...N(2)] out of the

Table 5. The mean endocyclic bond angles (°) for a few 1,2,3-triazole rings depicted in Fig. 1

| Angle at | 1 <i>H</i> -Triazoles | 1' <i>H</i> -Imidazole* | 2 <i>H</i> -Triazoles |
|-----------|-----------------------|-------------------------|-----------------------|
| N(1) | <111> | > <108> | > <103> |
| N(2) (CH) | <108> | < <113> | < <116> |
| N(3) | <108> | > <105> | > <103> |
| C(2) | <104> | ~ <104> | < <108> |

* In this column are the corresponding data of 4-amino-5-carbamoyl-1*H*-imidazole (*f* in Fig. 1) which differs from 5-amino-4-carbamoyl-1*H*-1,2,3-triazole by the replacement of N(2) with a CH group, and in the location of the tautomeric H atom (1*H* → 1'*H*). In a preliminary report (Kálmán & Simon, 1975) it was incorrectly described as 5-amino-3*H*-imidazol-4-carboxamide.

Table 6. *The parameters of the hydrogen bonds formed by the molecules*

| | N...X | H...X | N-H...X |
|-------------------------------|--------|--------|---------|
| N(1)-H...N(2)[1-x, ½+y, ½-z] | 2.87 Å | 2.02 Å | 165.4° |
| N(4)-H(42)...N(3)[x, y-1, z] | 3.03 | 2.32 | 133.0 |
| N(4)-H(41)*...O(2)[x, y-1, z] | 2.92 | 2.47 | 116.0 |
| N(4)-H(41)*...O(1)[x, y, z] | 2.91 | 2.36 | 124.9 |

* H(41) participates in both weak NH...O hydrogen bonds, which may thus be regarded as bifurcated hydrogen bonds. A similar bifurcated hydrogen bond was found in 5-amino-4-carbamoyl-1*H*-1,2,3-triazole (Kálmán *et al.*, 1974).

three intermolecular bridges (Table 6). Moreover, no dimers are formed. This phenomenon may perhaps be explained as follows. The dimer shown in Fig. 2(a) can be formed only by tautomers of the 1'*H*-type, e.g. 4-amino-5-carbamoyl-1*H*-imidazole. The 1*H*-tautomers, on the other hand, seem to prefer the dimer form shown in Fig. 2(b), which is excluded in the presence of an ethoxycarbonyl group. Any other theoretically possible

dimer, e.g. maintained by the N(1)-H...N(2) pair, would presumably lead to an even less compact crystal structure than that found in the title compound.

We thank Mr G. Lindahl (General Manager, Syntex, Analytical Instruments AB, Akersberga, Sweden) for his offer of collecting the data on the Syntex P2, automatic single-crystal diffractometer in our laboratory.

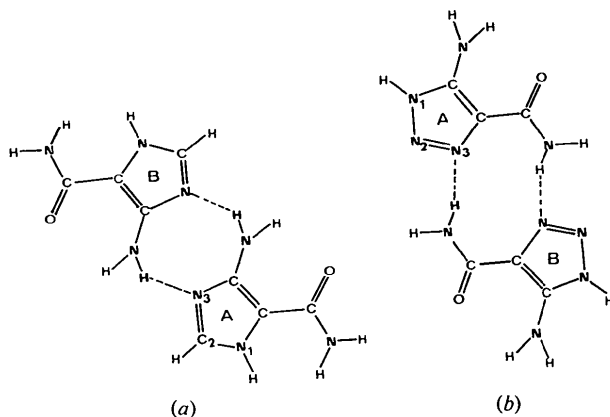


Fig. 2. The dimer pairs formed by the molecules of (a) 4-amino-5-carbamoyl-1*H*-imidazole and (b) 5-amino-4-carbamoyl-1*H*-1,2,3-triazole.

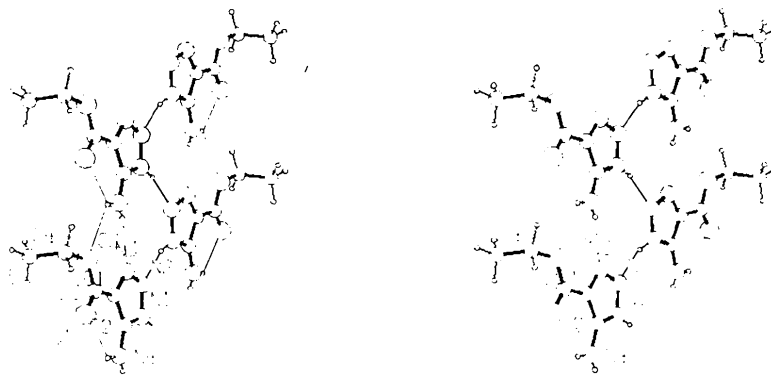


Fig. 3. A stereo drawing of the hydrogen-bond network formed around the 2₁ screw axes. The infinite sheets of molecules formed along **b** are independent of each other.

References

- CROMER, D. T. & LIBERMAN, D. (1970). *J. Chem. Phys.* **53**, 1891-1898.
- CROMER, D. T. & MANN, J. B. (1968). *Acta Cryst.* **A24**, 321-324.
- KÁLMÁN, A., PÁRKÁNYI, L. & SCHAWARTZ, J. (1977). *Acta Cryst.* **B33**, 3097-3102.
- KÁLMÁN, A., PÁRKÁNYI, L., SCHAWARTZ, J. & SIMON, K. (1976). *Acta Cryst.* **B32**, 2245-2247.
- KÁLMÁN, A. & SIMON, K. (1975). *Acta Cryst.* **A31**, S175.
- KÁLMÁN, A., SIMON, K., SCHAWARTZ, J. & HORVÁTH, G. (1974). *J. Chem. Soc. Perkin II*, pp. 1849-1852.
- KOKKOU, S. C. & RENTZEPEPIS, P. J. (1975). *Acta Cryst.* **B31**, 1564-1570.
- PINNER, A. (1895). *Ber. dtsh. chem. Ges.* **28**, 473-488.
- PURNELL, L. G., SHEPHERD, J. C. & HODGSON, D. J. (1975). *J. Amer. Chem. Soc.* **97**, 2376-2380.

- SCHAWARTZ, J., HORNYÁK (née HÁMORI), M. & SZÜTS, T. (1970). *Chem. Ind.* pp. 92–93.
- SCHOMAKER, V. & TRUEBLOOD, K. N. (1968). *Acta Cryst.* **B24**, 63–76.
- SHELDRIK, G. M. (1975). The *SHELX* crystal structure calculation program. Univ. of Cambridge, England.
- SIMON, K., SCHAWARTZ, J. & KÁLMÁN, A. (1977). *Cryst. Struct. Commun.* In the press.
- SLETTEN, J., SLETTEN, E. & JENSEN, L. H. (1968). *Acta Cryst.* **B24**, 1692–1698.
- STEWART, R. F., DAVIDSON, E. R. & SIMPSON, W. T. (1965). *J. Chem. Phys.* **42**, 3175–3187.

Acta Cryst. (1977). **B33**, 3106–3109

Crystal and Molecular Structure of the Trinuclear Chromium(III) and Iron(III) Complex, $[\text{Cr}_2\text{FeO}(\text{CH}_3\text{COO})_6(\text{H}_2\text{O})_3]\text{NO}_3 \cdot \text{CH}_3\text{COOH}$

BY T. GŁOWIAK, M. KUBIAK, T. SZYMAŃSKA-BUZAR AND B. JEŻOWSKA-TRZEBIATOWSKA

Institute of Chemistry, University of Wrocław, 50-383 Wrocław, Poland

(Received 1 March 1977; accepted 2 April 1977)

$[\text{Cr}_2\text{FeO}(\text{CH}_3\text{COO})_6(\text{H}_2\text{O})_3]\text{NO}_3 \cdot \text{CH}_3\text{COOH}$ is monoclinic, space group $P2_1/c$, with $a = 11.774$ (1), $b = 14.706$ (2), $c = 15.157$ (2) Å, $\beta = 90.70$ (1)°, $Z = 4$. The structure was refined to $R = 0.061$ with 2516 counter reflexions, for which $F > 3.92\sigma(F)$. The cation possesses idealized D_{3h} symmetry with the O in the centre of an equilateral triangle.

Introduction

Trinuclear coordination compounds containing three antiferromagnetically coupled Cr or Fe ions have recently been investigated theoretically and experimentally. Neither the mechanism of unpaired electron-spin interactions nor the factors affecting the magnitudes of these interactions have been established. For an interpretation of the magnetic properties in this group of compounds studies on mixed complexes with Cr_2FeO or Fe_2CrO groups, in which the ions of different electron configurations are coupled simultaneously, are important. Such compounds have been isolated (Weinland & Gussman, 1909) but only in recent years were they subjected to detailed structural studies.

Magnetic studies (Zelentsov, Zhemchuznikova, Rakitin, Yablokov & Yakubov, 1975) and EPR spectra (Yablokov, Gaponenko, Eremin, Zelentsov & Zhemchuznikova, 1973) confirmed the appearance of pure compounds with nuclei containing two types of metal atoms and showed that exchange interactions between the Fe atoms in mixed complexes are larger than in the Fe_3O group, whereas interpretation of the Cr–Cr interactions is not so well defined.

Measurements of the electronic spectra (Zelentsov, Zhemchuznikova & Lubovskii, 1975) carried out for mixed complexes do not enable any conclusions to be drawn as to the symmetry perturbations of the $M_2M'O$ group or of the nearest environment of each metal atom. In order to determine the structural details of a complex cation containing two types of metal atoms, an

X-ray investigation of the $[\text{Cr}_2\text{FeO}(\text{CH}_3\text{COO})_6(\text{H}_2\text{O})_3]\text{NO}_3 \cdot \text{CH}_3\text{COOH}$ complex was carried out.

Experimental

The compound was prepared as described by Zelentsov *et al.* (1975). Dark-red crystals suitable for X-ray studies were obtained by slow evaporation of an acetic acid solution. Weissenberg photographs showed the crystals to be monoclinic with systematic absences $0k0$, $k = 2n + 1$ and $h0l$, $l = 2n + 1$, which fix the space group uniquely as $P2_1/c$. Cell parameters were obtained by least squares from the setting angles of 15 reflexions measured on a diffractometer. The density was measured by flotation in a chloroform/bromoform mixture. Crystal data are listed in Table 1.

Intensities from a crystal $0.15 \times 0.15 \times 0.2$ mm were collected with Cu $K\alpha$ radiation on a Syntex $P2_1$ computer-controlled four-circle diffractometer with

Table 1. *Crystal data*

| | |
|---|--|
| $[\text{Cr}_2\text{FeO}(\text{CH}_3\text{COO})_6(\text{H}_2\text{O})_3]\text{NO}_3 \cdot \text{CH}_3\text{COOH}$. FW 706.3 | |
| Monoclinic, space group $P2_1/c$ | |
| $a = 11.774$ (1) Å | $Z = 4$ |
| $b = 14.706$ (2) | $\lambda(\text{Cu } K\alpha) = 1.5418$ Å |
| $c = 15.157$ (2) | $D_m = 1.78$ g cm ⁻³ |
| $\beta = 90.70$ (1)° | $D_c = 1.77$ |
| $V = 2624$ Å ³ | $\mu(\text{Cu } K\alpha) = 124$ cm ⁻¹ |