compounds. This difference is significantly larger than for coordination compounds with unsubstituted 1,2,4-triazole (Engelfriet, Groeneveld & Nap, 1980, and references cited therein). This indicates a more defined localization of the double-bond character between N1—C5 and N2—C3. The in-plane metal–metal distance is larger in the manganese compound. This effect can be ascribed to the larger ionic radius of Mn. Because of hydrogen bridges between the coordinating water molecules and the non-coordinating N2 of the triazole rings, the M—N(1)—N(2) angle is significantly smaller than the M—N(1)—C(5) angle. This effect, which has been observed earlier in some pyrazole-containing compounds (Reimann, Mighell & Mauer, 1967; Mighell, Reimann & Santoro, 1969), accounts for an additional lengthening of the metal–metal distance in $[Mn(btr)_2(H_2O)_2].H_2O$. The angle between the least-squares planes through the triazole rings is the same in the free ligand and in the three coordination compounds. The angle of about 90° prohibits any conjugation between the two rings. The absence of conjugation through the N4—N(substituent) or N4—C(substituent) bonds has been observed in other 4-substituted triazoles such as 4-amino-3,5-bis(pyridin-2-yl)-1,2,4-triazole (Key, de Graaff, Haasnoot & Reedijk, 1984) and 3-(2-hydroxyphenyl)-4-phenyl-1,2,4-triazole (van Roosmalen, Vreugdenhil, de Graaff, Haasnoot & Reedijk, 1987).

The anion vibrations in the infrared spectrum [*i.e.* 1760, 1410 (broad), 1050, 830, 730 cm^{-1}] are consistent with the non-coordinating behaviour of the nitrate groups. The ligand vibrations are similar to those of $[Co(NCS)_2(btr)_2].H_2O$, as might be expected because of the similarity between the two compounds. It is not clear why some splittings (at 1012 and 870 cm^{-1}), which were observed in the thiocyanate compound, do not appear.

Although btr is a potentially tetradentate ligand, the synthesis of coordination compounds with btr as a tetranucleating ligand have so far been unsuccessful.

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Tetrakis(2,6-dimethyl-4-pyridinone)zinc(II) Nitrate

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Abstract. $[Zn(C_7H_9NO)_4](NO_3)_2$, $M_r = 682$, orthorhombic, $Pbcn$, $a = 27.471$ (20), $b = 9.509$ (5), $c = 12.666$ (4) Å, $V = 3309$ (3) Å^3, $Z = 4$, $D_x = 1.37$ Mg m^{-3}, Mo $K\alpha$, $\lambda = 0.71069$ Å, $\mu = 0.831$ mm^{-1}, $F(000) = 1424$, $T = 291$ K, $R = 0.081$ for 1183 observed reflections. The Zn atom lies on a

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twofold axis and is tetrahedrally coordinated by the O atom of 2,6-dimethyl-4-pyridinone. Nitrate groups are not coordinated, but are hydrogen-bonded to the N of the ligand.

Introduction. Only a few complexes of 4-pyridinones and metal salts have been previously prepared and some of their structural data deduced from spectroscopic measurements (Cook, 1963; Tosato, Soccorsi & Cignitti, 1973; Sano, Sugitani & Nagashima, 1975). Complete structural determination seems particularly useful for complexes containing 2,6-dimethyl-4-pyridinone, owing to the ability of this compound to give the hydroxypyridine tautomer, so that nitrogen-coordination becomes theoretically possible. If we assume the pyridinone form, the N—H group can be hydrogen bonded, especially with oxygen-containing anions like NO_3^-; however, this is difficult to demonstrate by means of the usual physical methods.

2,6-Dimethyl-4-pyridinone is synthesized from 2,6-dimethyl-4-pyranone by standard procedures (Bellingham, Johnson & Katritzky, 1968). Hot ethanolic solutions of the nitrate metal salt and of the ligand were mixed together; on cooling, small white crystals of the complex appeared (melting point 529–531 K). Analytical data give the general formula $Zn(C_7H_9NO)_4(NO_3)_2$. In the infrared spectrum of the complex (solid, KBr disc), a band of medium intensity occurs at 1384 cm^{-1}. It can be indicative of an ionic nitrate (Nakamoto & McCarthy, 1968), but this assignment is not unambiguous, because the other bands expected for an ionic nitrate are masked by the ligand absorptions. Conductivity in methanol solution corresponded to a 2:1 electrolyte; this suggests that the nitrate anions are not coordinated. This is rather surprising because nitrate anions usually show rather strong coordination tendencies. In the literature, there are examples of complexes between metallic nitrates and organic ligands similar to the one we used: pyridine in $[(C_5H_5N)_2Zn(NO_3)_2]$ (Cameron & Taylor, 1971), and 2,6-dimethyl-4-pyranone in $[(C_7H_8O_2)_2Zn(NO_3)_2]$ (Brown & Lewis, 1984) and in $[(C_7H_8O_2)_2Cu(NO_3)_2]$ (Brown & Lewis, 1985). They all show nitrato groups coordinated to the metal.

The crystallographic study of this new compound therefore appeared to be the most convenient method of obtaining information about the part played by the nitrate anion in the crystal lattice.

Experimental. D_m not measured. Parallelepiped crystal with dimensions 0·13 × 0·13 × 0·27 mm. Lattice parameters refined using 15 reflections in the range $3 \leq 2\theta \leq 15°$. Syntex $P2_1$ diffractometer, graphite-monochromatized Mo $K\alpha$ radiation. 2458 *hkl* independent reflections with $(\sin\theta)/\lambda \leq 0{\cdot}561$ Å^{-1}, 1183 with $I \geq 2{\cdot}5\sigma(I)$. Standard reflection (232) checked every 50 reflections: no significant deviation. Structure solved by *SHELX*84 (Sheldrick, 1984), H atoms in computed positions. Anisotropic least-squares refinement (*SHELX*76; Sheldrick, 1976) on *F*; H isotropic with common refined temperature factor ($B = 15$ Å^2). $w = 1/(\sigma^2 + 0{\cdot}0007F^2)$, $R = 0{\cdot}081$, $wR = 0{\cdot}079$, $S = 3{\cdot}35$ for 1183 observed reflections. Final maximum shift-to-e.s.d. ratio = 0·42. Maximum and minimum heights in final difference Fourier synthesis = 0·56 and −0·47 e Å^{-3}. Atomic scattering factors from *International Tables for X-ray Crystallography* (1974). No corrections for absorption or secondary extinction.

Discussion. The atomic parameters are given in Table 1,* bond distances and angles in Table 2, and selected torsion angles (Klyne & Prelog, 1960) in Table 3. Fig. 1 shows the coordination of Zn and the numbering of the atoms (*PLUTO*; Motherwell & Clegg, 1978). Fig. 2 is a stereoscopic view showing the packing of $[Zn(C_7H_9NO)_4](NO_3)_2$.

Zn lies on a twofold axis and is tetrahedrally coordinated by the oxygen atoms of the pyridinone. The angles around the Zn atom are close to the ideal value for tetrahedral surroundings.

Bond lengths O9—Zn [1·96 (1)] and O18—Zn [1·90 (1) Å] are among the shortest that can be observed in tetrahedral zinc complexes (Brown & Lewis, 1984, and references therein).

The two pyridinone rings are almost planar, as can be seen from the torsion angles (Table 3). The mean distance of atoms from the plane of the ring is 0·021 Å (for the ring containing N1) and 0·016 Å (for the ring containing N10). The dihedral angle between the two planes for the pyridinone rings is about 80°. Deviation is markedly increased for the ring containing N1. Upon coordination, this ring shows asymmetric C—C and N—C bonds: C2—C3 [1·36 (2)]; C5—C6 [1·42 (2)]; N1—C2 [1·38 (1)]; N1—C6 [1·30 (1) Å]. The latter N—C bond is especially short, the usual N—C bond lengths in 4-pyridinones lying in the range 1·34–1·38 Å (Mostad, Romming & Rosenqvist, 1973). C4—O9 [1·26 (1) Å] is near the value observed for uncoordinated 4-pyridinones (C=O ≃ 1·27 Å) (Bailey *et al.*, 1983).

The second ring (N10C11C12C13C14C15) presents no significant distortion from C_{2v} symmetry; moreover, its angle values are about 120 (2)° and the C—C and N—C bonds have values close to 1·37 (1) Å. C13—O18 [1·36 (1) Å] lies in the same field. From these observations, it can be concluded that extensive

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* Lists of structure factors, anisotropic thermal parameters, H-atom coordinates and torsion angles have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 43940 (12 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Table 1. *Atomic coordinates* ($\times 10^4$) *and equivalent isotropic temperature factors* (Å^2) *with e.s.d.'s in parentheses*

$$B_{\rm eq} = \tfrac{8}{3}\pi^2 \textstyle\sum_i \sum_j U_{ij} a_i^* a_j^* \mathbf{a}_i . \mathbf{a}_j .$$

	x	y	z	$B_{\rm eq}$
N1	828 (3)	−3854 (10)	243 (8)	3·2 (2)
C2	950 (4)	−3141 (14)	1154 (11)	3·9 (3)
C3	634 (4)	−2134 (13)	1503 (10)	4·2 (3)
C4	204 (4)	−1770 (13)	936 (10)	3·2 (2)
C5	110 (3)	−2558 (13)	−5 (10)	2·7 (2)
C6	457 (5)	−3555 (14)	−352 (10)	4·1 (3)
C7	1401 (5)	−3554 (15)	1715 (11)	6·7 (4)
C8	388 (4)	−4430 (13)	−1349 (9)	4·5 (3)
C9	−90 (3)	−835 (9)	1243 (6)	4·2 (2)
C10	1927 (3)	1511 (11)	3419 (8)	3·7 (2)
C11	1571 (5)	799 (13)	3964 (10)	3·7 (3)
C12	1116 (4)	753 (12)	3540 (10)	3·4 (3)
C13	1010 (3)	1468 (12)	2627 (11)	3·0 (2)
C14	1365 (5)	2222 (12)	2115 (9)	3·8 (3)
C15	1826 (3)	2227 (12)	2497 (12)	3·3 (2)
C16	1720 (5)	71 (19)	4972 (11)	6·9 (3)
C17	2283 (4)	2986 (15)	2037 (10)	5·9 (3)
C18	550 (3)	1482 (8)	2230 (6)	4·2 (2)
C19	1816 (6)	−5927 (17)	−649 (9)	5·8 (3)
C20	2106 (3)	−6867 (12)	−902 (9)	7·1 (3)
C21	1986 (4)	−4704 (15)	−617 (12)	10·7 (4)
C22	1403 (3)	−6200 (11)	−358 (8)	6·3 (2)
Zn	0	332 (2)	$\frac{1}{4}$	3·9 (4)

Table 2. *Bond lengths* (Å) *and angles* (°) *with e.s.d.'s in parentheses*

C2—N1	1·38 (1)	C13—C12	1·37 (2)
C6—N1	1·30 (1)	O18—C13	1·36 (1)
C3—C2	1·36 (2)	C17—C15	1·56 (1)
C7—C2	1·48 (2)	O20—N19	1·24 (1)
C4—C3	1·43 (2)	O22—N19	1·22 (1)
C5—C4	1·43 (2)	O21—N19	1·25 (2)
O9—C4	1·26 (1)	C15—N10	1·38 (1)
C6—C5	1·42 (2)	C16—C11	1·51 (2)
C8—C6	1·52 (2)	C14—C13	1·37 (2)
Zn—O9	1·96 (1)	C15—C14	1·35 (1)
C11—N10	1·38 (1)	Zn—O18	1·90 (1)
C12—C11	1·36 (1)		

C6—N1—C2	125 (1)	C15—N10—C11	122 (1)
C7—C2—N1	118 (1)	C16—C11—N10	117 (1)
C4—C3—C2	122 (1)	C13—C12—C11	121 (1)
O9—C4—C3	123 (1)	O18—C13—C12	121 (1)
C6—C5—C4	119 (1)	C15—C14—C13	120 (1)
C8—C6—N1	117 (1)	C17—C15—N10	112 (1)
Zn—O9—C4	125 (1)	Zn—O18—C13	132 (1)
C3—C2—N1	118 (1)	O21—N19—O20	116 (2)
C7—C2—C3	124 (1)	O22—N19—O21	122 (1)
C5—C2—C3	116 (1)	O22—N19—O20	122 (2)
O9—C4—C5	121 (1)	C12—C11—N10	118 (1)
C5—C6—N1	120 (1)	C16—C11—C12	125 (1)
C8—C6—C5	123 (1)	C14—C13—C12	120 (1)
O9—Zn—O9	110·9 (5)	O18—C13—C14	119 (1)
O18—Zn—O18	109·6 (5)	C14—C15—N10	119 (1)
O18—Zn—O9	106·3 (3)	C17—C15—C14	128 (1)

Table 3. *Selected torsion angles* (°) (*e.s.d.'s* $\simeq 2°$)

C2—N1—C6—C5	−8	C11—N10—C15—C14	0
C2—C3—C4—C5	2	C11—C12—C13—C14	1
O9—C4—C5—C6	177	C11—C12—C13—O18	−177
C4—C5—C6—N1	8	C13—C14—C15—N10	−2

conjugation which includes the carbonyl group exists around the pyridinone ring.

Nitrate anions are not coordinated to the metal atom, the tetrahedral coordination sphere of Zn being complete with four neutral ligand molecules.

The complexes are linked together by means of hydrogen bonds involving two O atoms of a nitrate ion, as shown in Fig. 2. Every complex ion [Zn-(pyridone)$_4$]$^{2+}$ is surrounded by four ionic nitrates.

Hydrogen-bond distances and angles are given below:

N1—H···O22(x,y,z) = 2·84 Å, N1—H···O22 ≃ 176°,
N10—H···O20($\frac{1}{2}-x,-\frac{1}{2}-y,\frac{1}{2}+z$) = 2·81 Å, N10—H···O20 ≃ 168°.

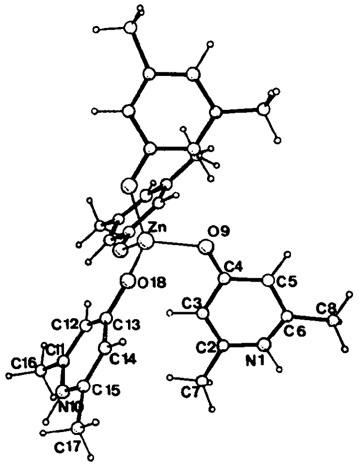

Fig. 1. Structure of the complex cation [Zn(C_7H_9NO)$_4$]$^{2+}$ showing the atom labelling.

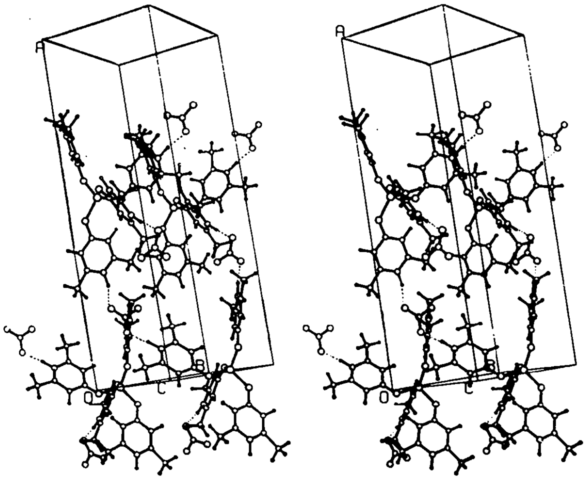

Fig. 2. Stereoscopic view of the unit cell. Dashed lines denote hydrogen bonds.

In the nitrate ion the longest N—O distance involves the O atom which is not hydrogen bonded (Table 2). Angles around the N atom show significant distortion from D_{3h} symmetry, due to hydrogen bonding.

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Structure of $[Fe_2(CO)_6\{\mu\text{-}C(SiMe_3)C(SiMe_3)CHCHCH(OEt)\}]$. An η^1, η^3-Allyl Bridged Diiron Complex

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Abstract. μ-1:2κ^2C^1-[5-Ethoxy-1,2-bis(trimethylsilyl)penta-2,4-dienyl]-1$\kappa^2C^{2,3}$;2$\kappa^2C^{4,5}$-bis(tricarbonyliron)(*Fe–Fe*), $[Fe_2(CO)_6(C_{13}H_{26}OSi_2)]$, $M_r = 534{\cdot}28$, triclinic, $P\bar{1}$, $a = 14{\cdot}594\,(4)$, $b = 10{\cdot}049\,(3)$, $c = 8{\cdot}776\,(3)$ Å, $\alpha = 79{\cdot}14\,(2)$, $\beta = 97{\cdot}61\,(2)$, $\gamma = 94{\cdot}84\,(2)°$, $V = 1250\,(1)$ Å^3, $D_x = 1{\cdot}419$ g cm^{-3}, $Z = 2$, $F(000) = 552$, $\lambda(\mathrm{Mo}\,K\alpha) = 0{\cdot}71069$ Å, $\mu(\mathrm{Mo}\,K\alpha) = 12{\cdot}86$ cm^{-1}, $T = 288$ K. The structure was solved by direct methods and refined by full-matrix least squares to $R = 0{\cdot}057$ for 3720 reflections. It consists of $Fe_2(CO)_6$ units linked by an organic bridge which results formally from the coupling of ethoxymethylidene, ethanediylidene and bis(trimethylsilyl)ethanediylidene radicals. The Fe—Fe length [2·625 (1) Å] is longer than those values usually observed in $Fe_2(CO)_6$ centres.

Introduction. The synthesis of the dinuclear anionic complexes $[Fe_2(CO)_6(\mu\text{-}CO)\{\mu\text{-}C(R)C(R)H\}^-]$ has opened up a new area in the extensive field of study of the reactivity of organic molecules at dinuclear centres. In this paper we describe the crystal and molecular structure of the compound resulting from the interaction of an $Fe_2(CO)_6(\mu\text{-}COEt)(\mu\text{-}CHCH_2)$ complex with bis(trimethylsilyl)acetylene.

Experimental. A poor-quality crystal ($0{\cdot}1 \times 0{\cdot}1 \times 0{\cdot}2$ mm), Philips PW 1100 diffractometer. Cell parameters from 25 reflections ($4 \leq \theta \leq 12°$) refined by least squares; graphite-monochromatized Mo $K\alpha$ radiation, ω-scan technique, scan width 1°, scan speed 0·03° s^{-1}. Three reflections every 2 h, no significant intensity decay observed. 3842 independent reflections ($2 \leq$

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