

Structure of Aquachloro[tris(2-aminoethyl)amine]nickel(II) Chloride Monohydrate

BY ARMANDO MARZOTTO

Dipartimento di Chimica Inorganica, Metallorganica ed Analitica, Università di Padova, Via Loredan 4, 35100 Padova, Italy

DORE AUGUSTO CLEMENTE

Dipartimento di Scienza dei Materiali, Facoltà di Scienze, Università di Lecce, Via Monteroni, 73100 Lecce, Italy

AND GIOVANNI VALLE

Centro di Studio sui Biopolimeri, CNR, Università di Padova, Via Marzolo 1, 35100 Padova, Italy

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Abstract. $[\text{Ni}(\text{C}_6\text{H}_{18}\text{N}_4)(\text{H}_2\text{O})\text{Cl}]\text{Cl}\cdot\text{H}_2\text{O}$, $M_r = 311.88$, monoclinic, $P2_1/a$, $a = 14.117(2)$, $b = 11.040(2)$, $c = 8.828(1)$ Å, $\beta = 106.8(2)^\circ$, $V = 1317(1)$ Å³, $Z = 4$, $D_x = 1.57$ Mg m⁻³, $\lambda(\text{Mo } K\alpha) = 0.7107$ Å, $\mu = 1.879$ mm⁻¹, $F(000) = 656$, $T = 293$ K, $R = 0.030$ for 2756 independent reflections [$F_o > 3\sigma(F_o)$]. The Ni atom is octahedrally surrounded by the four N atoms of the tren [tris(2-aminoethyl)amine] ligand, $\text{N}(\text{CH}_2\text{CH}_2\text{NH}_2)_3$, one chloride ion and one water molecule. The second chloride ion and the second water molecule are not bound to Ni^{II} and contribute only to the crystal packing stabilization. The title compound has also been characterized by thermogravimetric analysis and infrared spectroscopy. The results are discussed and examined in comparison to the electronic spectra and conductivity measurements in aqueous solution where the molecular structure is formulated differently as $[\text{Ni}(\text{C}_6\text{H}_{18}\text{N}_4)(\text{H}_2\text{O})_2]\text{Cl}_2$.

Introduction. The present investigation of the title compound was undertaken owing to its use as a starting material (Torres & Marzilli, 1991; Marzotto, Clemente, Ciccarese & Valle, 1993) in the synthesis of highly selective coordination complexes with DNA nucleobases (adenine, cytosine, guanine, etc.). The tetradentate tripodal tren ligand has been chosen because in octahedral complexes it can adopt only one geometry which has two *cis* sites free for bonding.

On the basis of electronic spectra in aqueous solution, Jørgensen (1956) suggested that the title compound should be formulated as $[\text{Ni}(\text{tren})(\text{H}_2\text{O})_2]\text{Cl}_2$. Therefore, in order to obtain further insight into coordination of the metal and the molecular structure, we have prepared and investigated in the solid state the title compound through

infrared and thermogravimetric measurements, culminating with the X-ray diffraction analysis, and have compared these results with the data obtained in aqueous solution through electronic spectra and conductivity measurements.

Experimental. X-ray diffraction intensities collected at 293 K through a Philips PW 1100 automated four-circle diffractometer with Mo $K\alpha$ graphite-monochromated radiation. Thermogravimetric measurements carried out with a Perkin-Elmer TGS-2 analyzer equipped with a Fourier-transform IR (Bruker IFS-66 spectrometer) for the detection of evolved gases. Infrared spectra measured as KBr pellets or Nujol mulls with a 5Sxc FT-IR (20F far ir) Nicolet spectrometer. Conductivity measurements were performed in doubly distilled water [$C = 4.0$ mol m⁻³ (4.0 mmol l⁻¹), $T = 302$ K] using an Amel model 134 instrument. UV-vis spectra recorded with a Lambda 15 Perkin-Elmer and a Beckman DK-2A spectrophotometer.

The title complex was prepared by reacting equimolar amounts (0.405 g, 1.70 mmol) of green $\text{NiCl}_2\cdot 6\text{H}_2\text{O}$ with tris(2-aminoethyl)amine (tren) [0.26 µm³ (0.26 ml), 1.70 mmol] in 20 µm³ (20 ml) of absolute ethanol. A microcrystalline blue powder was obtained after addition of diethyl ether and storing the solution at 243 K overnight. The solid was filtered and washed with absolute ethanol and diethyl ether, and dried under vacuum. Single blue crystals of the compound were obtained by slow recrystallization from ethanol. Analysis calculated for $\text{C}_6\text{H}_{22}\text{Cl}_2\text{N}_4\text{NiO}_2$: C 23.10, H 7.11, N 17.97, Cl 22.73%. Found: C 23.44, H 7.00, N 18.12, Cl 22.57%. A clear blue prism 0.26 × 0.26 × 0.32 mm was mounted on a glass capillary and coated slightly with diluted polystyrene cement. Cell

constants were refined based on 25 reflections in the 2θ range $18\text{--}20^\circ$; $\omega\text{--}2\theta$ scan mode, ω scan width 1.2° and scan speed $0.15^\circ \text{ min}^{-1}$; 5 s background measurements at both ends of a scan peak; three standard reflections remeasured at 100 reflection intervals; no significant intensity variation ($< \pm 0.1\%$); 3181 unique (3369 total, $R_{\text{int}} = 0.0422$) reflections were collected within $2\theta_{\text{max}} = 56.01^\circ$ ($\sin\theta/\lambda = 0.661 \text{ \AA}^{-1}$) ($h = 18$ to 17 , $k = 0$ to 14 , $l = 0$ to 11) and 2756 reflections with $F_o \geq 3\sigma(F_o)$ were used for structure determination. Intensities corrected for Lorentz and polarization, not for absorption or extinction. The structure was solved by the standard Patterson method and successive difference Fourier maps. Refinement by full-matrix least squares (on F) using anisotropic thermal parameters for non-H atoms and isotropic thermal parameters for H atoms (224 parameters refined) converged to $R = 0.030$ and $wR = 0.0389$ with $w = 1/[\sigma^2(F) + 0.0031F^2]$; maximum $\Delta/\sigma = 0.40$; $S = 0.95$. The highest peak in the final $\Delta\rho$ map had a height of 0.36 e \AA^{-3} ; the maximum negative peak had a height of -0.71 e \AA^{-3} . All calculations were performed with the *SHELX76* (Sheldrick, 1976) system and the molecular illustration was drawn using *ORTEP* (Johnson, 1976) on a VAX 8640 computer. Scattering factors are those incorporated in the *SHELX76* package. The final atomic fractional coordinates are reported in Table 1.*

Discussion. As mentioned above, the tetradentate tripod-like tren ligand bound to an Ni^{II} ion in an octahedral complex leaves two *cis* positions available for binding to other ligands such as imidazole or adenine nucleobase (Marzotto *et al.*, 1993). In the title complex the two *cis* positions are occupied by one chloride ion and one water molecule. Thus, the Ni atom lies at the centre of the nearly octahedral complex and is coordinated to the four N atoms of the tetradentate tren ligand, to a molecule of water and to one chloride ion.

The molecular structure and the atom-numbering scheme are illustrated in the *ORTEP* plot shown in Fig. 1. Bond distances and angles are listed in Table 2. Table 3 shows that the Ni—N distances for the known hexacoordinate Ni^{II} —tren complexes vary over a wide range [from $2.047(7)$ to $2.172(2) \text{ \AA}$]. Among the numerous factors responsible for this the following should be considered: (a) the electronic effects of the ligands in positions *trans* to the tren ligand; (b) the hydrogen-bonding pattern formed by

Table 1. Fractional coordinates with equivalent isotropic thermal parameters (\AA^2)

U_{eq} is defined as one third of the trace of the orthogonalized U_{ij} tensor.

	<i>x</i>	<i>y</i>	<i>z</i>	U_{eq}
Ni	0.28573 (2)	0.02382 (2)	0.87905 (3)	0.0252 (1)
Cl(1)	0.35464 (4)	-0.04317 (6)	1.14869 (7)	0.0401 (2)
Cl(2)	0.05426 (4)	0.18146 (5)	0.17082 (8)	0.0443 (2)
O(1) <i>W</i>	0.2507 (1)	-0.1708 (2)	0.8154 (2)	0.0410 (6)
O(2) <i>W</i>	0.4134 (2)	0.2061 (2)	1.3492 (3)	0.0508 (7)
N(10)	0.2232 (1)	0.0850 (2)	0.6455 (2)	0.0267 (5)
N(11)	0.4072 (1)	-0.0150 (2)	0.7924 (3)	0.0332 (6)
N(12)	0.3236 (1)	0.2073 (2)	0.9198 (2)	0.0328 (6)
N(13)	0.1405 (2)	0.0366 (2)	0.8931 (3)	0.0339 (6)
C(9)	0.3820 (2)	0.0076 (2)	0.6193 (3)	0.0380 (8)
C(10)	0.2705 (2)	0.0111 (2)	0.5470 (3)	0.0351 (7)
C(11)	0.2432 (2)	0.2169 (2)	0.6357 (3)	0.0346 (7)
C(12)	0.3314 (2)	0.2587 (2)	0.7704 (3)	0.0349 (6)
C(13)	0.1148 (2)	0.0619 (2)	0.6081 (3)	0.0363 (7)
C(14)	0.0788 (2)	0.0977 (2)	0.7487 (3)	0.0400 (7)

the tren N atoms; (c) the monomeric or dimeric nature of the complexes. The Ni^{II}—Cl(1) distance, $2.413(3) \text{ \AA}$, is slightly shorter than that found in $[\text{Ni}(\text{tren})(\text{AdH})\text{Cl}]\text{Cl}$, $2.531(3) \text{ \AA}$ (AdH = neutral adenine), whereas the Ni—O(1)*W* distance of the coordinated water molecule, $2.239(2) \text{ \AA}$, is longer than that found in $[\text{Ni}(\text{tren})(\text{ImH})(\text{H}_2\text{O})]\text{Cl}_2$, $2.156(3) \text{ \AA}$ (ImH = neutral imidazole) (Marzotto *et al.*, 1993) and appreciably larger than the Ni—O distance (about 2.0 \AA) for coordination of water to nickel (Duggan & Hendrickson, 1974). The other molecule of water and the other chloride ion, which is out of the metal coordination sphere, contribute only to the crystal packing stability through a complicated hydrogen-bond network. The shortest hydrogen bond is between O(2)*W* and Cl(2) [$\text{O}(2)\text{W}\cdots\text{H}\cdots\text{Cl}(2)^{\text{ii}} = 3.128(4) \text{ \AA}$] and this explains the relatively high loss temperature ($330\text{--}354 \text{ K}$) observed for this uncoordinated water molecule. Moreover, the Cl(2) ion is engaged in several other hydrogen bonds, they are: O(1)*W*—H \cdots Cl(2)ⁱ = $3.172(2) \text{ \AA}$; N(11)—H \cdots Cl(2)ⁱ = $3.395(2) \text{ \AA}$; N(12)—H \cdots Cl(2)ⁱⁱ = $3.585(7) \text{ \AA}$; N(13)—H \cdots Cl(2)ⁱⁱⁱ = $3.574(3) \text{ \AA}$; N(13)—H \cdots Cl(2)^{iv} = $3.431(4) \text{ \AA}$ [(i) $\frac{1}{2} - x, -\frac{1}{2} + y, 1 - z$; (ii) $\frac{1}{2} + x, \frac{1}{2} - y, 1 + z$; (iii) $-x, -y, 1 - z$; (iv) $x, y, 1 + z$].

The X-ray structure is in agreement with thermogravimetric data confirming that the two water molecules are chemically non-equivalent. In fact, the TG curve shows their loss occurs in two steps. The first dehydration takes place between 330 and 354 K with a mass loss of 5.50% (5.78% theoretical) and the second occurs between 371 and 387 K with a mass loss of 5.91% (5.78% theoretical).

The evolved gas was also identified as water vapour by its vibrational and rotational spectra. Finally, from 387 to 553 K no mass loss is observed, indicating formation of the intermediate stable species $\text{Ni}(\text{tren})\text{Cl}_2$. Also, the $[\text{Ni}(\text{py})(\text{tren})(\text{H}_2\text{O})]\text{X}_2$

* Lists of structure factors, anisotropic thermal parameters and H-atom parameters have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 55909 (19 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England. [CIF reference: NA1022]

complexes ($X = \text{Cl, Br, I}$; $\text{py} = \text{pyridine}$) give $\text{Ni}(\text{tren})\text{X}_2$ as the final product of the thermal reaction (Ihara & Sakura, 1988).

The IR frequencies of the $[\text{Ni}(\text{tren})(\text{H}_2\text{O})\text{Cl}]\text{Cl}\cdot\text{H}_2\text{O}$ complex in comparison with the free tren ligand are summarized in Table 4. Considerable changes are observed in particular in the $3377\text{--}3171\text{ cm}^{-1}$ (NH_2 and OH stretchings), $2983\text{--}2857\text{ cm}^{-1}$ (C--H stretching) regions and the $1632\text{--}1539\text{ cm}^{-1}$ (NH_2 bending), $1323\text{--}1024\text{ cm}^{-1}$ (NH_2 and CH_2 vibrations and C--N stretching) regions. The distortion from a perfectly octahedral symmetry should produce up to four infrared-active metal-nitrogen stretching vibrations for Ni--N . In fact, $\nu(\text{Ni--N})$ are observed at $354s$, $320w$, $292w$ and $262sh\text{ cm}^{-1}$, $\nu(\text{Ni--OH}_2)$ at $361m\text{ cm}^{-1}$ and $\nu(\text{Ni--Cl})$ at $241m\text{ cm}^{-1}$, in agreement with our previous results (Marzotto *et al.*, 1993). In contrast, in aqueous solutions the presence of the $[\text{Ni}(\text{tren})(\text{H}_2\text{O})_2]^{2+}$ cation and two Cl^- anions is supported by molar conductivity measurements which give a value $\Lambda = 24.4\text{ mS m}^2\text{ mol}^{-1}$ ($244\text{ }\Omega^{-1}\text{ cm}^2\text{ mol}^{-1}$), corresponding to a 2:1 electrolyte. These results are perfectly consistent with the formulation of $[\text{Ni}(\text{tren})(\text{H}_2\text{O})_2]\text{Cl}_2$ for this Ni complex in aqueous solution, in agreement also with the suggestions of Jørgensen (1956).

The electronic UV-vis spectrum exhibits the same features observed by other authors for *cis*- $[\text{Ni}(\text{tren})\text{X}_2]$ complexes (Burke, Richardson & McCarthy, 1984; Lever, 1985; Ihara & Sakura,

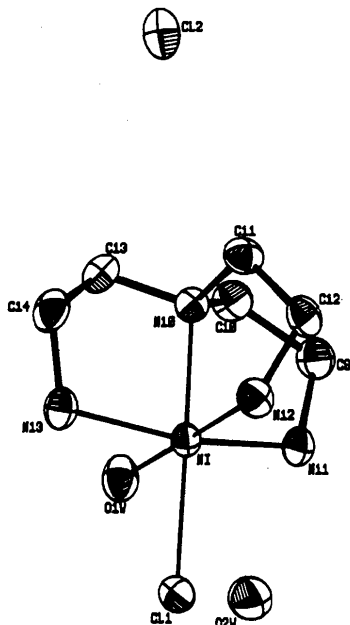


Fig. 1. ORTEP drawing of the $[\text{Ni}(\text{tren})(\text{H}_2\text{O})\text{Cl}]\text{Cl}\cdot\text{H}_2\text{O}$ complex with the numbering scheme used. H atoms are omitted for clarity.

Table 2. Bond distances (\AA) and angles ($^\circ$) for $[\text{Ni}(\text{tren})(\text{H}_2\text{O})\text{Cl}]\text{Cl}\cdot\text{H}_2\text{O}$

Ni—Cl(1)	2.413 (3)	Ni—O(1)W	2.239 (2)
Ni—N(10)	2.105 (3)	Ni—N(11)	2.114 (3)
Ni—N(12)	2.100 (2)	Ni—N(13)	2.095 (2)
N(10)—C(10)	1.484 (3)	N(10)—C(11)	1.491 (3)
N(10)—C(13)	1.491 (3)	N(11)—C(9)	1.486 (4)
N(12)—C(12)	1.469 (3)	N(13)—C(14)	1.482 (4)
C(9)—C(10)	1.519 (4)	C(11)—C(12)	1.524 (4)
C(13)—C(14)	1.524 (4)		
N(12)—Ni—N(13)	97.5 (2)	N(11)—Ni—N(13)	161.0 (1)
N(11)—Ni—N(12)	93.7 (1)	N(10)—Ni—N(13)	84.0 (2)
N(10)—Ni—N(12)	82.67 (8)	N(10)—Ni—N(11)	82.2 (1)
O(1)W—Ni—N(13)	86.0 (2)	O(1)W—Ni—N(12)	174.5 (2)
O(1)W—Ni—N(11)	81.8 (1)	O(1)W—Ni—N(10)	93.57 (9)
Cl(1)—Ni—N(13)	94.9 (1)	Cl(1)—Ni—N(12)	96.69 (8)
Cl(1)—Ni—N(11)	99.0 (1)	Cl(1)—Ni—N(10)	178.61 (8)
Cl(1)—Ni—O(1)W	87.16 (6)	Ni—N(10)—C(13)	106.0 (2)
Ni—N(10)—C(11)	109.7 (2)	Ni—N(10)—C(10)	105.4 (2)
C(11)—N(10)—C(13)	110.7 (2)	C(10)—N(10)—C(13)	112.5 (2)
C(10)—N(10)—C(11)	112.2 (3)	Ni—N(11)—C(9)	111.1 (3)
Ni—N(12)—C(12)	107.5 (2)	Ni—N(13)—C(14)	108.8 (3)
N(11)—C(9)—C(10)	110.3 (3)	N(10)—C(10)—C(9)	110.8 (2)
N(10)—C(11)—C(12)	112.1 (2)	N(12)—C(12)—C(11)	109.1 (2)
N(10)—C(13)—C(14)	109.8 (3)	N(13)—C(14)—C(13)	109.4 (3)

Table 3. Comparison of some significant Ni—N distances (\AA) in hexacoordinate Ni^{II} -tren complexes

	Ni—N(10)	Ni—N(11)	Ni—N(12)	Ni—N(13)	Ni—N (mean)
$[\text{Ni}(\text{tren})(\text{H}_2\text{O})\text{Cl}]\text{Cl}\cdot\text{H}_2\text{O}^a$	2.105 (3)	2.114 (3)	2.100 (2)	2.095 (2)	2.104 (3)
$[\text{Ni}(\text{tren})(\text{ImH})(\text{H}_2\text{O})\text{Cl}_2]\text{Cl}_2\cdot\text{H}_2\text{O}^b$	2.088 (6)	2.115 (5)	2.118 (7)	2.115 (5)	2.109 (6)
$[\text{Ni}(\text{tren})(\text{AdH})\text{Cl}]\text{Cl}^c$	2.104 (3)	2.076 (3)	2.113 (3)	2.111 (3)	2.101 (3)
$[\text{Ni}(\text{tren})](\text{NCS})_2^d$	2.104 (3)	2.145 (4)	2.090 (4)	2.132 (4)	2.118 (4)
$[\text{Ni}_2(\text{tren})_2(\text{trien})](\text{ClO}_4)_2^e$	2.087 (5)	2.140 (9)	2.125 (6)	2.156 (18)	2.127 (10)
$[\text{Ni}_2(\text{tren})_2(\text{N}_3)_2](\text{BPh}_4)_2^f$	2.078 (6)	2.117 (6)	2.067 (5)	2.079 (6)	2.085 (6)
$[\text{Ni}_2(\text{tren})_2(\text{C}_6\text{O}_6\text{Cl}_2)](\text{BPh}_4)_2^g$	2.085 (4)	2.109 (4)	2.058 (4)	2.141 (5)	2.098 (4)
$[\text{Ni}_2(\text{tren})_2](\text{OCN})_2(\text{BPh}_4)_2^h$	2.130 (7)	2.047 (7)	2.054 (5)	2.095 (7)	2.081 (7)
$[\text{Ni}(\text{tren})_2](\text{BF}_4)_2^i$	2.172 (2)	—	2.129 (2)	2.145 (3)	2.149 (2)

References: (a) present paper; (b), (c) Marzotto, Clemente, Ciccarese & Valle (1993); (d) Santarsiero & Schomaker (1983); (e) Willett (1983); (f) Pierpont, Francesconi, Duggan, Wagner & Barefield (1975); (g) Pierpont, Francesconi & Hendrickson (1977); (h) Duggan & Hendrickson (1974); (i) Colpas, Kumar, Day & Maroney (1990).

Table 4. Infrared spectra (cm^{-1}) of free tren and $[\text{Ni}(\text{tren})(\text{H}_2\text{O})\text{Cl}]\text{Cl}\cdot\text{H}_2\text{O}$

tren ^a ligand	$[\text{Ni}(\text{tren})(\text{H}_2\text{O})\text{Cl}]\text{Cl}\cdot\text{H}_2\text{O}$	Band assignment
3350s, 3270s	3377sh, 3334sh, 3281ms, 3256sh	$\nu(\text{NH}_2)$, $\nu(\text{O--H})$
3180m	3171sh	
2930s, 2855s, 2800s	2983w, 2932w, 2888w, 2857w	$\nu(\text{C--H})$
1590s, ^b	1632w, 1596m, 1539vw	$\delta(\text{NH}_2)_{\text{sym}}$
1455m, 1390w, 1365sh, 1348m	1474m, 1455m, 1431vw, 1397w, 1357w, 1344w	$\delta(\text{CH}_2)$, $\gamma(\text{CH}_2)$
1304m, 1270m, 1230w	1323w, 1314w, 1286w, 1262w, 1247w, 1234w	$\delta(\text{NH}_2)_{\text{sym}}$, $\gamma(\text{NH}_2)$, $(\text{CH}_2)_{\text{twist}}$
1090m, 1070w, 1035s, 1020sh	1163w, 1118w, 1078s, 1061w, 1053w, 1041w, 1024s	$\gamma(\text{NH}_2)$, $\nu(\text{C--N}) + (\text{NH}_2)_{\text{twist}}$
902s, ^b , 865s, ^b , 840sh	993vw, 978m, 897vw, 880m, 850w	$(\text{NH}_2)_{\text{twist}}$, $\rho(\text{CH}_2)$
765sh, 730w	745m, 718w, 670m, 650m, 608w, 592vw, 570sh, 550m, 542m, 470w, 451w, 400w, 361m	$\rho(\text{NH}_2)$, $\nu(\text{Ni--OH}_2)$, $\nu(\text{Ni--N})$, $\nu(\text{Ni--Cl})$
	354sh, 320w, 292w, 262sh, 241m, 233m	

Reference: (a) Ficheux & Morris (1978).

1988). The three characteristic broad bands (one in the near-IR region, $27\,700\text{ cm}^{-1}$, and the other two in the visible region, at $17\,700$ and $10\,500\text{ cm}^{-1}$, respectively) support a distorted octahedral geometry in solution, owing to a d^8 ion in a nearly octahedral field. A spin forbidden band (${}^3A_{2g} \rightarrow {}^1E_g$) is observable as a shoulder near $12\,800\text{ cm}^{-1}$. Finally the broad character of the bands indicates the presence of low-symmetry components in the ligand field (Lever, 1982).

In conclusion, the X-ray analysis demonstrates unequivocally that the structure of the present compound in the solid state must really be formulated as $[\text{Ni}(\text{tren})(\text{H}_2\text{O})\text{Cl}]\text{Cl}\cdot\text{H}_2\text{O}$, whereas in aqueous solution, although the *cis* conformation is maintained (Marzotto *et al.*, 1993), it should be represented as $[\text{Ni}(\text{tren})(\text{H}_2\text{O})_2]\text{Cl}_2$.

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A New Tetranuclear Iron(III) Complex with an $[\text{Fe}_4\text{O}_2]$ Core: Synthesis, Structure and Mössbauer Studies of $[\text{Fe}_4(\mu_3\text{-O})_2(\mu\text{-O}_2\text{CCH}_3)_6\text{Cl}_2(3\text{-Mepy})_4]\cdot\text{CH}_3\text{C}\equiv\text{N}$ (3-Mepy = 3-Methylpyridine)

BY L. WU, M. PRESSPRICH AND P. COPPENS*

Department of Chemistry, State University of New York at Buffalo, Buffalo, New York 14214, USA

AND M. J. DEMARCO

Department of Physics, State University College at Buffalo, Buffalo, New York 14222, USA

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Abstract. Hexakis(μ -acetato)bischlorotetrakis(3-methylpyridine)bis(μ_3 -oxo)tetrairon(III) acetonitrile, $[\text{Fe}_4\text{Cl}_2(\text{C}_2\text{H}_3\text{O}_2)_6\text{O}_2(\text{C}_6\text{H}_7\text{N})_4]\cdot\text{C}_2\text{H}_3\text{N}$, $M_r = 1094.1$, triclinic, $P\bar{1}$, $a = 11.236(2)$, $b = 11.709(3)$, $c = 19.897(4)\text{ \AA}$, $\alpha = 75.55(2)$, $\beta = 81.02(1)$, $\gamma = 78.92(2)^\circ$, $V = 2471(1)\text{ \AA}^3$, $Z = 2$, $D_x = 1.471\text{ g cm}^{-3}$, $\lambda(\text{Mo K}\alpha) = 0.71073\text{ \AA}$, $\mu = 13.2\text{ cm}^{-1}$, $F(000) = 1124$, room temperature, $R = 0.045$ for 6551 reflections with $I > 3\sigma(I)$. The title compound contains a

tetrairon core linked by bridging oxygen and acetate ions. Each of the octahedrally coordinated iron(III) atoms is bonded to 3-methylpyridine, three μ -acetates and at least one μ_3 -oxygen. Two Fe atoms are also coordinated by chlorides while the other two are additionally coordinated by another μ_3 -oxygen. Mössbauer results indicate two quadrupole splittings in accordance with the two types of iron coordination spheres. The quadrupole splittings of 1.04 and 0.67 mm s^{-1} are assigned to the chloride- and non-chloride-bonded Fe atoms, respectively.

* Author to whom correspondence should be addressed.

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