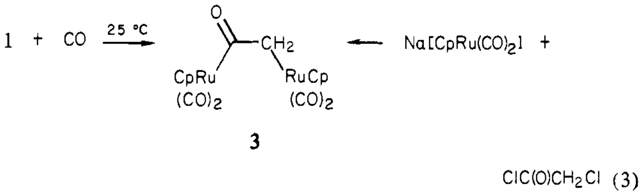
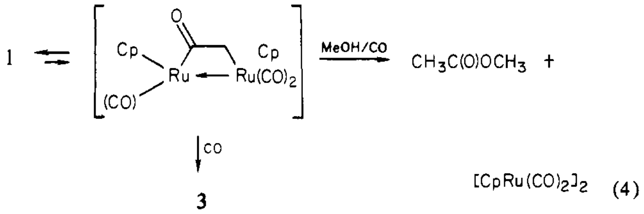
from Na[CpRu(CO)$_2$] and ClCH$_2$C(O)Cl. The bridging acyl[9] has a ν_{CO} at 1622 cm^{-1} and a ^{13}C NMR resonance at 236.7 ppm. Similarly, we find that a trimethylphosphine substituted analogue of **3**, [CpRu(PMe$_3$)(CO)](μ-C(O)CH$_2$)[CpRu(CO)$_2$] (**4**),[10] was formed from the reaction of **1** with excess PMe$_3$ at room temperature. **1** reacts with methanol and CO at room temperature,



(3)

affording methyl acetate and [CpRu(CO)$_2$]$_2$. If CO is absent, methyl acetate is still formed, but **2** is produced as a byproduct. The complex Fe$_2$(CO)$_8$(μ-CH$_2$) reacts similarly.[11] Presumably, an MC(O)CH$_2$M intermediate is formed and methanolyzed in both cases. Since **3** is unaffected by methanol, we suggest that methyl acetate is formed by methanolysis of an unsaturated intermediate derived by CO insertion into the Ru–CH$_2$ bond of **1** (eq 4). Consistent with this proposal we observed that photolysis



(4)

of **3** in methanol affords methyl acetate. The rapid insertion of CO into the Ru–C bond of **1** is remarkable. The Ru-alkyl derivatives CpRu(CO)$_2$CH$_2$X (X = H, OMe, OC(O)R) react only slowly with CO at 1000 psi and above 100 °C.[12]

The dimeric ruthenium complexes [CpRu(CO)$_2$]$_2$(μ-CH$_2$)$_n$ (n = 2, **5**; n = 3, **6**; n = 4, **7**) have been prepared from 1,2-dichloroethane, 1,3-dibromopropane, 1,4-dibromobutane and Na[CpRu(CO)$_2$] for comparison.[13] These complexes are considerably more stable than **1**. When heated above 70 °C or photolyzed, **5** eliminates ethylene.[14] The complex **6** is converted to an equimolar mixture of CpRu(CO)$_2$H and CpRu(CO)(η-C$_3$H$_5$) under UV irradiation.[13b]

These observations establish that (1) μ-methylene complexes do not require metal-metal bonds or other bridging ligands for stability, (2) lack of these structural features significantly modifies reactivity, and (3) formation of methyl acetate from **1** and Fe$_2$(CO)$_8$(μ-CH$_2$) likely proceeds by methanolysis of coordinatively unsaturated intermediates containing MC(O)CH$_2$M fragments.

Acknowledgment. We thank E. A. Conaway and L. Lardear for their skilled technical assistance.

Supplementary Material Available: Summary of X-ray diffraction data (Table I), atomic positional (Table II) and thermal (Table III) parameters, bond lengths (Table IV) and bond angles (Table V), and a listing of the observed and calculated structure factors (20 pages). Ordering information is given on any current masthead page.

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(8) ^{1}H NMR (C$_6$D$_6$) δ 4.88 (5 H, s), 4.62 (5 H, s), 2.95 (2 H, s); ^{13}C NMR (C$_6$D$_6$) δ 202.54 (CO), 202.20 (CO), 90.42 (C$_5$H$_5$), 88.30 (C$_5$H$_5$), 27.2 (CH$_2$, J_{C-H} = 136.5 Hz), 236.70 (C=O).

(9) See, for example: Dyke, A. F.; Knox, S. A. R.; Naish, P. J.; Taylor, G. E. *J. Chem. Soc., Dalton Trans.* **1982**, 1297.

(10) ^{1}H NMR (C$_6$D$_6$) δ 4.96 (5 H, s), 4.78 (5 H, s), 3.13 (2 H, d), 1.19 (9 H, d, J_{P-H} = 10.0 Hz); ^{13}C NMR δ 258.28 (C=O, J_{C-P} = 13.1 Hz), 206.61 (C≡O, J_{C-P} = 20.1 Hz), 202.65 (C≡O), 202.45 (C≡O), 88.39 (C$_5$H$_5$) and 88.17 (C$_5$H$_5$), 26.92 (CH$_2$, J_{C-H} = 132.0, $J_{C-H'}$ = 137.0 Hz), 21.11 (PMe$_3$, J_{C-P} = 32.9 Hz); IR (hexane) 2022 (s), 1968 (s), 1928 (s), 1568 cm^{-1} (m, br). Anal. Calcd (found): C, 40.45 (40.18); H, 3.90 (3.93).

(11) Roper, M.; Strutz, H.; Keim, W. *J. Organomet. Chem.* **1981**, *219*, C5.

(12) Y. C. Lin and S. S. Wreford, unpublished results.

(13) The complexes [CpFe(CO)$_2$]$_2$[μ-(CH$_2$)$_n$] (n = 3, 4, and 5) have been previously prepared: (a) King, R. B. *Inorg. Chem.* **1963**, *2*, 531. (b) King, R. B.; Braitsch, D. M., *J. Organomet. Chem.* **1973**, *54*, 9. (c) Cooke, M.; Forrow, N. J.; Knox, S. A. R. *Ibid.* **1981**, *222*, C21.

(14) Other C$_2$H$_4$-bridged complexes are known and decompose by elimination of ethylene: Beck, W.; Olgemöller, B. *J. Organomet. Chem.* **1977**, *127*, C45.

Preparation and Characterization of Novel μ_3-N$_2$ Mixed Metal Complexes[1]

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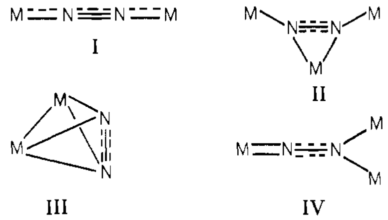
Received December 6, 1982

Extensive studies on the reactions of coordinated dinitrogen have shed some light on the mechanism for its reduction into ammonia and hydrazine under mild conditions.[2] Previously we reported that ligating dinitrogen in molybdenum and tungsten complexes *cis*-[M(N$_2$)$_2$(PMe$_2$Ph)$_4$] (**1**, M = Mo or W) are reduced stepwise into nitrogen hydrides via diazenido (M=N=N—H) and hydrazido(2–) (M=N—NH$_2$) complexes, which are formed by the electrophilic attack of proton on the terminal nitrogen.[3] These findings have led us to expect that treatment of dinitrogen complexes with some kinds of Lewis acids instead of a proton may form μ_2- or μ_3-N$_2$ complexes (metallodiazenido or hydrazido(2–) complexes) in which two different metals are bonded to each nitrogen atom.



Several types of polynuclear μ-N$_2$ complexes are already known. Many μ-N$_2$ complexes with a linear M-N-N-M moiety (type I) such as [(NH$_3$)$_5$RuN$_2$Ru(NH$_3$)$_5$][(BF$_4$)$_4$],[4] {MoCl$_4$[ReCl(PMe$_2$Ph)$_4$(N$_2$)]$_2$},[5] and [TaCl(C$_2$H$_4$)(PMe$_3$)$_3$]$_2$(μ-N$_2$)[6] have been prepared, the latter of which reacts with acetone to give dimethylketazine. An end-on bonded and sideways bonded dinitrogen ligand of type II has been found in a triply bridged dinitrogen complex of titanium with (μ_3-N$_2$)[(η^5:η^5-C$_{10}$H$_8$)(η-C$_5$H$_5$)$_2$Ti$_2$][(η^1:η^5-C$_5$H$_4$)(η-C$_5$H$_5$)$_3$Ti$_2$] unit.[7] Novel polynuclear dinitrogen complexes of nickel such as [(PhLi)$_6$Ni$_2$(N$_2$)(Et$_2$O)$_2$]$_2$[8]

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(1) Preparation and Properties of Molybdenum and Tungsten Dinitrogen Complexes. 18. For part 17 of this series, see: Hidai, M.; Yokotake, I.; Takahashi, T.; Uchida, Y. *Chem. Lett.* **1982**, 453–454.

(2) (a) Chatt, J.; Dilworth, J. R.; Richards, R. L. *Chem. Rev.* **1978**, *78*, 589–624 and references therein. (b) Hidai, M.; Mizobe, Y. "Reactions of Coordinated Ligand"; Plenum Press: New York, in press, and references cited therein.

(3) Takahashi, T.; Mizobe, Y.; Sato, M.; Uchida, Y.; Hidai, M. *J. Am. Chem. Soc.* **1980**, *102*, 7461–7467.

(4) (a) Harrison, D. F.; Weissberger, E.; Taube, H. *Science (Washington, D.C.)* **1968**, *159*, 320. (b) Treitel, I. M.; Flood, M. T.; Marsh, R. E.; Gray, H. B. *J. Am. Chem. Soc.* **1969**, *91*, 6512–6513. (c) Chatt, J.; Nikolsky, A. B.; Richards, R. L.; Sanders, J. R. *J. Chem. Soc., Chem. Commun.* **1969**, 154–155.

(5) Cradwick, P. D.; Chatt, J.; Crabtree, R. H.; Jeffery, E. A.; Richards, R. L. *J. Chem. Soc., Chem. Commun.* **1975**, 351–352.

(6) Turner, H. W.; Fellmann, J. D.; Rockage, S. M.; Shrock, R. R.; Churchill, M. R.; Wasserman, H. J. *J. Am. Chem. Soc.* **1980**, *102*, 7809–7811.

(7) Pez, G. P.; Apgar, P.; Crissey, R. K. *J. Am. Chem. Soc.* **1982**, *104*, 482–490.

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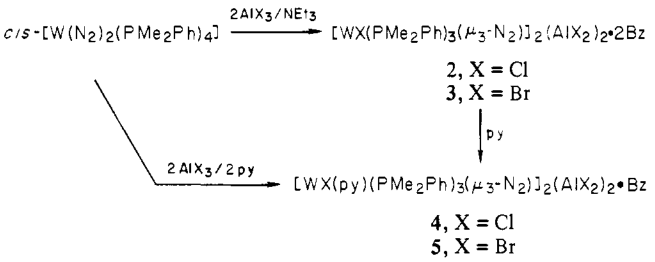
Table I. Physical Properties of μ_3-N_2 Complexes and a Related Complex

formula	color	mp,[a] °C	yield, %	notable bands,[b] cm^{-1}	ν(WCl), cm^{-1}
2, $[WCl(PMe_2Ph)_3(\mu_3\text{-}N_2)]_2(AlCl_2)_2\cdot 2Bz$	yellow	105	78	1392 s, 1338 s	258
4, $[WCl(py)(PMe_2Ph)_3(\mu_3\text{-}N_2)]_2(AlCl_2)_2\cdot Bz$	red	96	50	1400 s, 1350 s	256
3, $[WBr(PMe_2Ph)_3(\mu_3\text{-}N_2)]_2(AlBr_2)_2\cdot 2Bz$	golden-yellow	98	51	1375 s, 1318 s	
5, $[WBr(py)(PMe_2Ph)_3(\mu_3\text{-}N_2)]_2(AlBr_2)_2\cdot Bz$	dark red	77	60	1388 s, 1338 s	
6, $[WCl(py)(NN(H)AlCl_2)(PMe_2Ph)_3]$	dark red	51	39	3050 s, br[c]	

[a] All compounds decomposed at mp. [b] These bands are associated with $\nu(N_2)$; KBr disk; s strong, br broad. [c] This band is assigned to ν(NH).

Scheme I



2, X = Cl
3, X = Br

4, X = Cl
5, X = Br

contain a different type of sideways bridged dinitrogen ligand (type III). We describe here the first example of tungsten–aluminum complexes with triply end-on bridged dinitrogen ligand of type IV.

The novel μ_3-N_2 complexes $[WX(PMe_2Ph)_3(\mu_3\text{-}N_2)]_2(AlX_2)_2\cdot 2Bz$ (**2** X = Cl, **3** X = Br) are prepared in moderate yields by treatment of the dinitrogen complex **1** (M = W) with 2 mol equiv of AlX_3 followed by addition of 1 mol equiv of NEt_3 in benzene.[9] Treatment of the dinitrogen complex with 2 mol equiv of AlX_3 followed by addition of 2 mol equiv of pyridine yields $[WX(Py)(PMe_2Ph)_3(\mu_3\text{-}N_2)]_2(AlX_2)_2\cdot Bz$ (**4**, X = Cl; **5**, X = Br), which are also synthesized from **2** or **3** by addition of 1 mol equiv of pyridine. Analytical data of these complexes were satisfactory. The infrared spectra of these μ_3-N_2 complexes show strong bands in the region of 1320–1400 cm^{-1} (Table I), which shift to lower frequencies on ^{15}N labeling and are therefore associated with $\nu(N_2)$. The bands are shifted to lower frequencies when X is changed from Cl to Br. Coordination of pyridine (py) to the tungsten shifts the bands to higher frequencies (Scheme I).

The molecular structure of the complex **4** has been determined by X-ray crystallographic analysis.[11] A stereoview of the complex is shown in Figure 1, showing that the N_2 ligand is bound to one tungsten atom and two aluminum atoms. The W–N–N linkage is essentially linear, and a chloride anion occupies the position trans to the N_2 ligand. The W2–N3 and N3–N4 distances are rather different from the W1–N1 and N1–N2 distances, although the W1–N2 and W2–N4 distances are quite similar. Unusual thermal parameters for N1 and N3 probably make their positions ambiguous. Therefore, it is difficult to discuss the N–N distance compared with other dinitrogen complexes. However, it is to be noted that the bands associated with $\nu(N_2)$ are lower than those observed for any other dinitrogen complex except the titanium dinitrogen complex described above and for alkyldiazenido complexes such as $[MoI(N_2Me)(dppe)_2]$ (1543 cm^{-1})[12] and a BPh_3 adduct of a diazenido complex $[WHBrCl(N_2H(\rightarrow BPh_3))(PMe_2Ph)_3]$ (1450 cm^{-1}).[3] In the molecule of **4**, two aluminum atoms and two nitrogen atoms form a four-membered ring, where the average angle of N–Al–N is 88 (1)° and the average distance of Al–N is 1.85 (3) Å. Two tungsten, four nitrogen, and two aluminum atoms almost lie in the same plane.

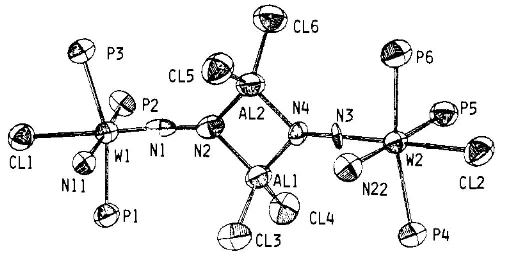
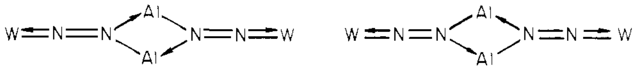


Figure 1. Persepctive view of $[WCl(Py)(PMe_2Ph)_3(\mu_3\text{-}N_2)]_2(AlCl_2)_2\cdot Bz$. The shapes of the atoms in this drawing represent 50% probability contours of thermal motions. The distances of W1–N2, W2–N4, N1–N2, and N3–N4 are 3.10 (3), 3.07 (3), 1.46 (4), and 1.25 (3) Å, respectively. The angles of W1–N1–N2 and W2–N3–N4 are 175 (2) and 178 (2)°, respectively.

The meridional configuration of the phophine ligands is consistent with the ^1H NMR spectrum, which shows two triplets and a doublet assigned to the methyl groups of PMe_2Ph. The complex may be regarded as a dimer of a singly bent metallo diazenido complex containing the $\mathrm{W}\overset{\leftarrow}{=}\mathrm{N}{=}\mathrm{N}{-}\mathrm{AlCl_2}$ moiety and described as a combination of two resonance structures:



Complexes **2–5** are considered to retain the dimeric structure in benzene since the IR spectra of the solutions show characteristic bands due to $\nu(N_2)$ in the region essentially similar to those for the compounds in the solid state.

The formation of adducts between Al(III) Lewis acids and dinitrogen complexes is already well-known. For example, an adduct, $[Mo(N_2AlEt_3)_2(PMe_2Ph)_4]$, of the complex **1** (M = Mo) with $AlEt_3$ exhibits $\nu(N_2)$ bands at 1850 and 1938 cm^{-1}, which are lower than those of the parent dinitrogen complex (1940 and 2025 cm^{-1}).[13] Previously Chatt et al. reported that an adduct of the dinitrogen complex **1** (M = W) with $AlCl_3$ decomposed and did not mention the structure.[14] Complexes **2–5** obtained here are completely different from the simple adducts since (1) one molecule of dinitrogen ligand is released as gas, (2) the parent

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(8) Kruger, C.; Tsay, Y.-H. *Angew. Chem., Int. Ed. Engl.* **1973**, *12*, 998–999.

(9) The reaction of **1** (M = W) with 1 mol equiv of AlX_3 (X = Cl or Br) seems to give $[WX(PMe_2Ph)_4(\mu_3\text{-}N_2)]_2(AlX_2)_2$. The latter complexes reacted with water in benzene to produce $[WX(NNH_2)(PMe_2Ph)_4]X^{10}$ in high yields. No pure complexes were isolated from the dark red solution obtained by treating **1** (M = W) with only 2 mol equiv of AlX_3 in benzene, although the IR spectrum of the solution showed notable bands at 1480, 1390, and 1350 cm^{-1}. The color of the solution turned light red on adding NEt_3 to the solution. The resulting mixture, which precipitated the yellow μ_3-N_2 complex **2** as crystals by addition of hexane, exhibited notable bands at 1390 and 1340 cm^{-1} in its IR spectrum.

(10) Chatt, J.; Pearman, A. J.; Richards, R. L. *J. Chem. Soc., Dalton Trans.* **1978**, 1766–1776.

(11) The complex crystallized in the triclinic space group $P\bar{1}$ with cell dimensions a = 14.226 (5) Å, b = 25.141 (12) Å, c = 11.911 (4) Å, α = 103.84 (4)°, β = 99.78 (3)°, γ = 78.36 (4)°, and V = 4019.72 $Å^3$. Diffraction data were collected on Rigaku four-circle diffractometer; 7925 reflections ($|F_o| \geq \sigma|F_o|$) were used in the structure solution and refinement, where Lorentz, polarization, and analytical absorption corrections were made. The programs used for this analysis were UNICS system, and all calculations were done by a Hitac M-280H/M-200H computer. Since the crystal was not good, the final residuals were R = 0.136 and R_w = 0.129, from using block-diagonal least squares with anisotropic thermal parameters for non-hydrogen atoms except two nitrogen atoms in two pyridine rings.

(12) (a) Day, V. W.; George, T. A.; Iske, S. D. A. *J. Am. Chem. Soc.* **1975**, *97*, 4127–4128. (b) Chatt, J.; Diamantis, A. A.; Heath, G. A.; Hooper, N. E.; Leigh, G. J. *J. Chem. Soc., Dalton Trans.* **1977**, 688–697.

(13) Aresta, M. *Gazz. Chim. Ital.* **1972**, *102*, 781–792.

(14) Chatt, J.; Crabtree, R. H.; Jeffery, E. A.; Richards, R. L. *J. Chem. Soc., Dalton Trans.* **1973**, 1167–1172.

dinitrogen complex is not recovered on treatment with base, and (3) a halide anion of AlX_3 is transferred to the tungsten metal.

On treatment of complex **4** with 1 mol equiv of HCl gas in benzene, an aluminum hydrazido(2−) complex $[WCl(py)(NN(H)AlCl_2)(PMe_2Ph)_3]Cl$, **6**, is isolated as crystals in moderate yield. The complex shows a broad and strong band at 3050 cm^{-1} assigned to ν(NH) in the IR spectrum, suggesting hydrogen bonding between the N-H group and Cl anion.

Further studies are now in progress to develop the idea of activation of dinitrogen on multimetallic centers.

Supplementary Material Available: Tables of atomic positional and thermal parameters (4 pages). Ordering information is given on any current masthead page.

Unique High-Spin–Low-Spin Transition of the Central Ion in a Linear, Trinuclear Iron(II) Triazole Compound

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Received November 24, 1982

A variety of iron(II) compounds is known to show transitions from the high-spin ($S = 2$) state to the low-spin ($S = 0$) state upon cooling or upon increasing pressure.[1] A very strong ligand field is required to induce such a transition, and usually the transition is observed in Fe(II) compounds with chelating nitrogen donor ligands such as phenanthroline, dipyridyl, and 2,2′-pyridylimidazole.[1-3] In only a few cases such HS–LS transitions[4] have been observed with monodentate ligands in compounds $Fe(L)_6(anion)_2$, i.e., in isoxazole[5] and tetrazole[6] coordination compounds. Dinuclear and polynuclear Fe(II) compounds with strong-field ligands have not yet been reported to exhibit such transitions.

We recently prepared[7] a series of new trinuclear triazole compounds of the general formula $M_3(Rtr)_6(H_2O)_6(CF_3SO_3)_6$ (M = Mn, Fe, Co, Ni, or Zn, R is an alkyl group, and tr is 1,2,4-triazole). The structure of these compounds consists of linear trinuclear cations $[(H_2O)_3M(Rtr)_3M(Rtr)_3M(OH_2)_3]^{6+}$ and the triflate counterions.[7] The ligand-field spectra of the Co(II) and Ni(II) compounds indicate the presence of a strong ligand field in these compounds. Because of the asymmetric environment of the terminal metal ions and the expected strong ligand field, which affects the central ion, we have studied the iron compounds in detail to investigate the possibilities of HS–LS transitions. The results described below show that the central iron ion indeed changes its spin state upon cooling.

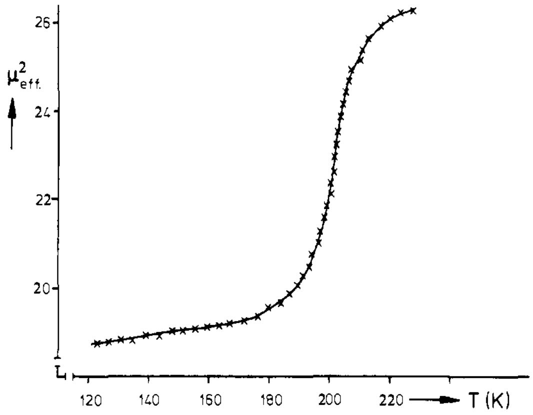

Figure 1. Plot of μ_{eff}^2 (μ in μ_B/mol of Fe) of $[Fe_3(4\text{-}Ettr)_6(H_2O)_6](CF_3SO_3)_6$ as a function of temperature.

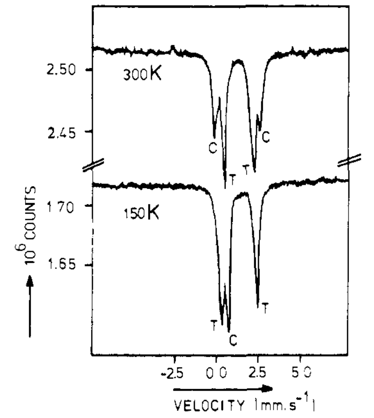

Figure 2. Mössbauer spectra at 300 and 150 K of $[Fe_3(4\text{-}Ettr)_6(H_2O)_6](CF_3SO_3)_6$; T refers to terminal iron; C refers to central iron.

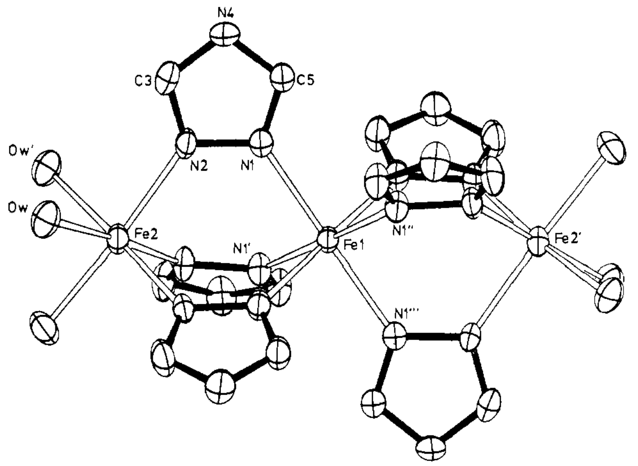

Figure 3. ORTEP drawing of the $[Fe_3(4\text{-}Ettr)_6(H_2O)_6]^{6+}$ cation showing the 50% probability ellipsoids. Hydrogen atoms and the ethyl groups have been omitted for clarity. Selected distances and angles are given in the table. The structure shown is the one obtained at 300 K; the low-temperature structure is essentially similar, apart from changes in bond lengths and angles. The triflate anions are hydrogen bonded to the water molecules (not shown in the figure).

The compound $[Fe(4\text{-}Ettr)_2(H_2O)_2]_3(CF_3SO_3)_6$ was easily prepared from aqueous solutions of the salt and the ligand.[8,9] Infrared spectra show the presence of uncoordinated triflate ions, and coordinated 4-ethyltriazole and water. The ligand-field spectrum recorded[10] at room temperature shows a broad band at 11 300 cm^{-1}, in agreement with high-spin Fe(II). Upon cooling to liquid-nitrogen temperature, the compound changes from white to purple and an additional band at 18000 cm^{-1} is observed in the diffuse reflectance spectrum. The presence of this additional band suggests low-spin Fe(II).[11] The magnetic susceptibility of the compound as a function of temperature[12] is depicted in Figure

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(1) Gütlich, P. *Struct. Bonding (Berlin)* **1981**, *44*, 82-195.

(2) König, E. *Coord. Chem. Rev.* **1968**, *3*, 471-495.

(3) Goodwin, H. A. *Coord. Chem. Rev.* **1976**, *18*, 293-325.

(4) Abbreviations used: HS = high spin; LS = low spin; tr = 1,2,4-triazole; Et = ethyl.

(5) Driessen, W. L.; Van der Voort, P. H. *Inorg. Chim. Acta* **1977**, *21*, 217-222.

(6) Franke, P. L.; Haasnoot, J. G.; Zuur, A. P. *Inorg. Chim. Acta* **1982**, *59*, 5-9.

(7) Vos, G. Ph.D. Thesis, State University Leiden, in preparation.

(8) In a typical preparation 0.01 mol of $Fe(H_2O)_6(CF_3SO_3)_2$ in 10 mL of H_2O containing a trace of HO_3SCF_3 was added to 0.03 mol of 4-ethyltriazole in 10 mL of water. Almost white crystals appear upon standing.[9]

(9) The compound correctly analyzes as $Fe(C_{10}H_{18}F_6O_8S_2N_6)$ (C,H,N,S,F). The compound is named as bis[triaquatris(4-ethyltriazole-N^1)-iron(II)-N^2,$N^{2\prime}$,$N^{2\prime\prime}$]iron(II) hexakis(trifluoromethylsulfonate).

(10) Obtained as the solid-state diffuse reflectance spectrum on a Beckman DK-2A with MgO as a reference.

(11) Low-spin Fe(II) species with a FeN_6 chromophore have bands at about 17000–19000 cm^{-1} in most cases.[1-3]

0002-7863/83/1505-1682$01.50/0