# Analysis of Multiply Charged Oxo-Bridged Complexes by Electrospray Ionization Mass Spectrometry

**Ulla N. Andersen, Christine J. McKenzie, and Gustav Bojesen***

Department of Chemistry, Odense University, DK-5230 Odense M, Denmark

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Twenty-one multiply charged oxobridged complexes with $\mu_2$-oxo and/or $\mu_2$-*O*,,*O*′-oxoacid bridges, have been characterized by electrospray ionization mass spectrometry (ESMS). No fragmentation was observed and in most cases the base peak could be assigned to the intact cationic complex (two to four charges). In a few cases the mass spectra indicated the lability in solution of these particular complexes. Other prominent peaks could be assigned to adducts between the cationic complex and the counter ion. The spectra supply clear-cut evidence for the nuclearity of all the complexes and, in general, enabled an unambiguous determination of the oxidation state of the metal centers and the composition of the bridges.

## Introduction

Electrospray (ES) ionization mass spectrometry as introduced by Fenn and co-workers[1] has opened the possibility of analyzing multiply-charged ions. The technique is now widely used in biopolymer analysis, but it has been shown by Kebarle and co-workers[2] that it also provides a way of characterizing multiply-charged inorganic complexes.

The present work is concerned with the characterization of oxo-bridged dinuclear complexes. Dinuclear iron, manganese, vanadium, and chromium complexes containing oxo bridges with a variety of terminal capping ligands have been prepared in our laboratory.[3] These compounds are significant in the study of magnetic exchange interactions[4] and have more recently become important as models for the active sites of a variety of metalloenzymes. The oxo-bridged iron and manganese complexes, in particular, are structural models for the oxo-bridged diiron active sites in the non-heme oxygen-carrying and activating enzymes, hemerythrin, ribonuclease reductase, and purple acid phosphatases and manganese clusters are found in the Mn-catalases and the manganese-containing oxygen evolution center (OEC) in photosystem II.[5]

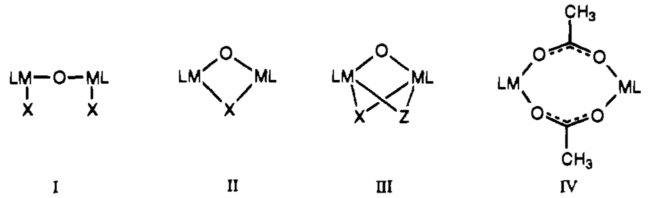

**Figure 1.** Core structures of the binuclear complexes used in this work. L represents a capping tetradentate or tridentate ligand: (**I**) a single ($\mu_2$-oxo)-bridged core, X represents terminal ligands e.g. water, chloride, and oxo; (**II**) a doubly-bridged core in which the $\mu_2$-oxo bridge is supported by a second bridging group, X (X may be a second $\mu_2$-oxo group or a $\mu_2$-*O*,*O*′-oxoanion, e.g. carboxylate, sulfate, phosphate, and carbonate); (**III**) a triply-bridged core in which the $\mu_2$-oxo bridge is supported by two bridging groups, X and Z (in some cases X = Z, X and Z may be a second $\mu_2$-oxo group or a $\mu_2$-*O*,*O*′-$CH_3CO_2^-$); (**IV**) a doubly $\mu_2$-*O*,*O*′-$CH_3CO_2^-$-bridged core structure.

The isolation of either oxo-bridged dinuclear or larger polyoxometallic aggregates[6] from reaction mixtures is often fortuitous and is controlled, only to some extent, by the choice of capping ligand. As a consequence, in many cases the characterization of oxo-bridged complexes is hindered by difficulties in establishing the nuclearity. The question of nuclearity is often only resolved by X-ray crystallography which is time consuming and requires the growth of suitable crystals. In the absence of a crystal structure the characterization of oxo-bridged complexes relies on "sporting methods" which are often inconclusive in the decision of formulation. These include, the measurement of magnetic susceptibility where magnetic moments, lower than the "spin-only" values appropriate for the constituent metal ions are generally observed, and spectroscopic methods such as infrared, resonance Raman, and UV−visible spectroscopy. Unfortunately, the presence of organic ligands can provide a multitude of additional bands which often makes the identification of the various frequencies difficult and very subjective. Nuclear magnetic resonance (NMR) spectroscopy is often of limited use, since many of the complexes are paramagnetic.

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* To whom correspondence should be addressed.

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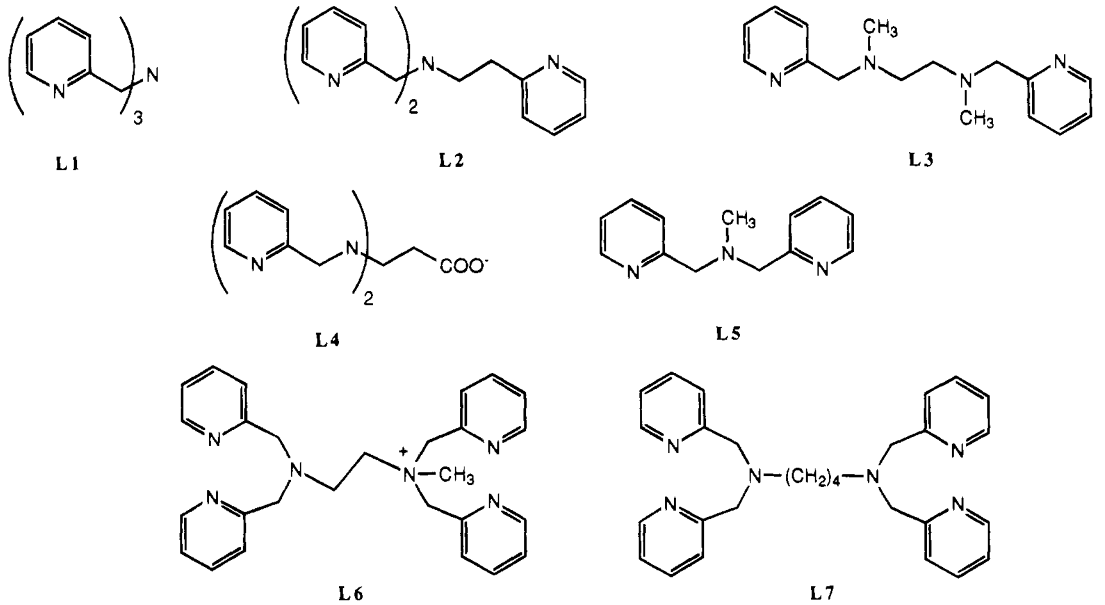

**Figure 2.** Aminopyridyl capping ligands used: **L1**, tris(2-pyridylmethyl)amine; **L2**, *N,N'*-bis(2-pyridylmethyl)-2-(2-pyridylethyl)amine; **L3**; *N,N'*-bis(2-pyridylmethyl)-*N,N'*-dimethyl-1,2-ethanediamine; **L4**, *N*-bis(2-pyridylmethyl)-3-aminopropionate; **L5**, *N,N'*-bis(2-pyridylmethyl)methylamine; **L6**, *N,N,N',N'*-tetrakis(2-pyridylmethyl)-*N*-methyl-1,2-ethanediamine cations; **L7**, *N,N'*-tetrakis(2-pyridylmethyl)-1,4-butanediamine.

## Experimental Section

The preparation and characterization of the complexes is described elsewhere.[3] Mass spectra were recorded on a Finnigan TSQ 700 triple quadrupole instrument equipped with a Finnigan API source operating in the electrospray mode. In this source the ions are desolvated in a heated capillary. The typical conditions were as follows: sample concentrations, 0.1 mM in CH$_3$CN (HPLC grade); flow rate, 5 $\mu$L/min, capillary potential, 4.5 kV; sheath gas; 40 psi. The temperature of the heated capillary was critical for the appearance of the spectra. For some of the compounds the spectra recorded with a capillary temperature of 50 °C showed the formation of adducts with CH$_3$CN. At higher temperatures these ions were not observed. The spectra were recorded by scanning the $m/z$ range between 40 and 2000 in 3 s. The data such as shown in Figure 3 were typically obtained by averaging 10–20 spectra.

## Results and Discussion

The core structures for the complexes studied here are illustrated in Figure 1. The complexes may contain a single $\mu_2$-oxo bridge, **I**, or alternatively the $\mu_2$-oxo bridge may be supported by either one or two bridging groups, **II** and **III** respectively. In the complexes presented here the supporting bridging groups are bidentate oxo–acido ligands such as carboxylates, phosphates and sulfates. One complex incorporating the bis($\mu$-*O,O'*-acetato) core, **IV**, is also included in the study.

We have previously shown that fast atom bombardment (FAB) mass spectrometry is a very useful method for characterization of singly- and doubly-charged inorganic complexes[7] and although some FAB mass spectral data have been reported for triply-bridged complexes,[8] in our hands, it has generally not been possible to generate stable ion currents from oxo-bridged complexes. It seems that the cores of singly- and doubly-bridged complexes are too fragile to withstand the conditions under the FAB ionization. This has prompted us to investigate the potential of electrospray ionization mass spectrometry (ESMS) for characterization of this important class of inorganic complexes and our results are presented below.

A summary of the main results is shown in Table 1. Structures of the tetradentate and tridentate capping ligands are given in Figure 2. A typical spectrum is shown in Figure 3. For 11 of the compounds X-ray crystallographic analyses are available.[3a–f,9] As is illustrated by Figure 3 the spectra have generally only a few peaks and they are easily assigned to the cationic complex, clusters of the complex with the counteranion, and the free (protonated) ligand. Very dilute solutions give rise to very intense signals (the spectra were recorded from 0.1 mM solution) and we have seen very little evidence of fragment ions. The inserts in Figure 3 illustrate that the resolution, even with a quadrupole instrument, is sufficient to determine the formal charge of the complex cations and provide a check of the isotopic patterns. With the symmetric compounds it is essential for a correct assignment of the peaks that the charge state of the ions can be determined. The spectrum of complex **18** shown in Figure 3 illustrates this. When the ligand and metal are known there are two possible assignment to the peak $m/z$ 340.9: LMnO$^+$ or L$_2$Mn$_2$O$_2$$^{2+}$. However, from the fits of the isotopic patterns shown it is clear that the peak can be assigned to a doubly-charged ion. Additionally, the peak at $m/z$ 682.2 can be assigned to a singly-charged ion. The data summarized in Table 1 demonstrate that the spectra supply clearcut evidence for the nuclearity of the all the complexes examined and, in general, the spectra also enable an unambiguous determination of the oxidation state of the metal centers and the composition of the bridges between them.

Adducts formed from the complex cation and the counter anion are observed for a number of the complexes with **7** being the most noticeable. These peaks provide a very useful check on the charge-state of the complex, in particular in the case of **7** where the resolution of the quadrupole mass spectrometer is insufficient to resolve the isotopic peaks of the quadruply charged complex ion. The crystal structure of complex **16** shows that this complex is tetranuclear, with two aminopyridyl ligands, L7, strapping between two ($\mu_2$-oxo)bis($\mu_2$-acetato)-bridged diiron(III) cores (**III**, Figure 1);[3d] consequently, the complex cation is quadruply charged. The peak for the 4+ ion

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**Table 1.** Electrospray Mass Spectral Data for Oxo-Bridged Complexes **1–21**

| complexes and conditions[a] | ions and peaks[b] | | |
|---|---|---|---|
| **1**, II | $X^{3+}$ | 242.4 | 100% |
| $[LFe^{III}O(CH_3CO_2)Fe^{III}L](ClO_4)_3$ | $X(ClO_4)^{2+}$ | 413.2 | 15% |
| ref 3c | $X(ClO_4)_2{}^+$ | 925.1 | 3% |
| L: L3 | $[LFe^{III}(CH_3CO_2)]_2O^{2+}$ | 393.3 | 22% |
| **2**, II* | $X^{3+}$ | 255.9 | 100% |
| $[LFe^{III}O(CH_3CO_2)Fe^{III}L](ClO_4)_3$ | $X(ClO_4)^{2+}$ | 433.2 | 15% |
| ref 9 | $X(ClO_4)_2{}^+$ | 965.0 | 3% |
| L: L1 | $[LFe^{III}(CH_3CO_2)]_2O^{2+}$ | 413.2 | 4% |
| *t*: 150 °C | | | |
| **3**, II* | | | |
| $[LFe^{III}O(CH_3CO_2)Fe^{III}L](ClO_4)$ | $X^+$ | 727.2 | 100% |
| ref 3a | | | |
| L: L4 | | | |
| *t*: 50 °C | | | |
| **4**, II | | | |
| $[LFe^{III}O(CH_3CO_2)Fe^{III}L](ClO_4)_3$ | $X^{3+}$ | 265.3 | 62% |
| ref 3h | $LH^+$ | 305.2 | 100% |
| L: L2 | $[LFe^{III}(CH_3CO_2)]_2O^{2+}$ | 427.3 | 50% |
| *t*: 150 °C | | | |
| **5**, II | $X^{3+}$ | 237.7 | 100% |
| $[LFe^{III}O(HCO_2)Fe^{III}L](ClO_4)_3$ | $X(ClO_4)^{2+}$ | 406.1 | 20% |
| ref 3c | $X(ClO_4)_2{}^+$ | 911.7 | 1% |
| L: L3 | $[LFe^{III}HCO_2)]_2O^{2+}$ | 378.9 | 40% |
| *t*: 150 °C | $[LFe^{III}(HCO_2)]_2O(ClO_4)^+$ | 857.2 | 1% |
| **6**, III* | | | |
| $[LFe^{III}O(CH_CO_2)_2Fe^{III}L](ClO_4)_2$ | $X^{2+}$ | 336.2 | 100% |
| ref 3h | $X(ClO_4)^+$ | 771.1 | 2% |
| L: L5 | | | |
| *t*: 50 °C | | | |
| **7**, III* | $X^{4+}$ | 281.1 | 35% |
| $\{LFe^{III}O(CH_3CO_2)_2Fe^{III}L](ClO_4)_4$ | $X(ClO_4)^{3+}$ | 408.0 | 25% |
| ref 3h | $X(ClO_4)_2{}^{2+}$ | 661.6 | 2% |
| L: L6 | $X(ClO_4)_3{}^+$ | 1421.0 | <1% |
| *t*: 150 °C | $L^+$ | 439.3 | 100% |
| **8**, II* | $LH^{2+}$ | 220.1 | 22% |
| $[LFe^{III}O(CO_3)Fe^{III}L](ClO_4)_2$ | $X^{2+}$ | 364.2 | 100% |
| ref 3c | $X(ClO_4)^+$ | 827.1 | 2% |
| L: L3 | | | |
| *t*: 50 °C | | | |
| **9**, II | $X^{2+}$ | 402.1 | 100% |
| $[LFe^{III}O(SO_4)Fe^{III}L](ClO_4)_2$ | $X(ClO_4)^+$ | 903.0 | 2% |
| ref 3b | $LH^+$ | 291.2 | 6% |
| L: L1 | | | |
| *t*: 50 °C | | | |
| **10**, II | $X^{2+}$ | 382.2 | 100% |
| $[LFe^{III}O(SO_4)Fe^{III}L](ClO_4)_2$ | $X(ClO_4)^+$ | 863.1 | <1% |
| ref 3c | $LH^+$ | 271.2 | 8% |
| L: L3 | | | |
| *t*: 50 °C | | | |
| **11**, II* | $X^{3+}$ | 319.4 | 100% |
| $[LFe^{III}O((C_6H_5O)_2PO_2)Fe^{III}L](ClO_4)_3$ | $X(ClO_4)^+$ | 528.4 | 7% |
| ref 9 | $LH^+$ | 291.2 | 8% |
| L: L1 | | | |
| *t*: 50 °C | | | |
| **12**, I | $X^{2+}$ | 369.2 | 100% |
| $[L(Cl)Fe^{III}OFe^{III}(Cl)L](ClO_4)_2$ | $X(ClO_4)^+$ | 837.1 | 2% |
| ref 3c | | | |
| L: L3 | | | |
| *t*: 50 °C | | | |
| **13**, I* | $X^{2+}$ | 389.2 | 100% |
| $[L(Cl)Fe^{III}OFe^{III}(Cl)L](ClO_4)_2$ | $X(ClO_4)^+$ | 878.9 | 2% |
| ref 3b | $LH^+$ | 291.2 | 1% |
| L: L1 | | | |
| *t*: 50 °C | | | |
| **14**, IV* | $X^{2+}$ | 385.2 | 100% |
| $[LFe^{II}(CH_3CO_2)_2Fe^{II}L](ClO_4)_2$ | $LFe^{III}O(CH_3CO_2)Fe^{III}L^{2+}$ | 363.7 | 40% |
| ref 3c | $[LFe^{III}(CH_3CO_2)]_2O^{2+}$ | 393.1 | 20% |
| L: L3 | | | |
| *t*: 150 °C | | | |
| **15**, I* | $[LFe^{III}OFe^{III}L]^{2+}$ | 334.1 | 100% |
| $[L(H_2O)Fe^{III}OFe^{III}(H_2O)L](ClO_4)_2$ | $[LFe^{III}OFe^{III}L]_2(ClO_4)^{3+}$ | 478.5 | 14% |
| ref 3b | $LFe^{III}OFe^{III}L(ClO_4)^+$ | 767.1 | 4% |
| L: L4 | | | |
| *t*: 150 °C | | | |

**Table 1** (Continued)

| complexes and conditions[a] | ions and peaks[b] | | |
|---|---|---|---|
| **16**,[c] III | $X^{4+}$ | 349.2 | 100% |
| $[L_2Fe^{III}_4O_2(CH_3CO_2)_4](NO_3)_4$ | $X(NO_3)^{3+}$ | 486.2 | 42% |
| ref 3d | $X(NO_3)_2{}^{2+}$ | 760.3 | 10% |
| L: L7 | $LH^+$ | 453.2 | 32% |
| *t*: 50 °C | | | |
| **17**, III* | $X^{3+}$ | 241.1 | 7% |
| $[LMn^{III}O(CH_3CO_2)Mn^{III}L](ClO_4)_3$ | $LMn^{III}(O)_2Mn^{III}L^{2+}$ | 341.2 | 100% |
| ref 3e | $LMn^{III}(O)_2Mn^{III}L(ClO_4)^+$ | 781.4 | 4% |
| L: L3 | $LMn^{III}(O_2)Mn^{IV}L^{3+}$ | 227.4 | 37% |
| *t*: 150 °C | $LH^+$ | 271.1 | 5% |
| **18**, II | $X^+$ | 682.2 | 100% |
| $[LMn^{III}(O)_2Mn^{IV}L](ClO_4)$ | $LMn^{IV}(O)_2Mn^{IV}L^{2+}$ | 340.9 | 25% |
| ref 3h | | | |
| L: L4 | | | |
| *t*: 150 °C | | | |
| **19**, II | $X^{3+}$ | 227.5 | 100% |
| $[LMn^{III}(O)_2Mn^{IV}L](ClO_4)_3$ | $X(ClO_4)_2{}^+$ | 881.4 | 14% |
| ref 3f | $LMn^{III}(O)_2Mn^{III}L^{2+}$ | 341.2 | 40% |
| L: L3 | $LMn^{III}(O)_2Mn^{III}L(ClO_4)^{2+}$ | 781.4 | 6% |
| *t*: 150 °C | $LH^+$ | 271.0 | 13% |
| **20**, I | $X^{2+}$ | 379.2 | 100% |
| $[L(O)V^{IV}OV^{IV}(O)L](ClO_4)_2$ | $X(ClO_4)^+$ | 857.4 | <1% |
| ref 3h | $LH^+$ | 305.2 | 4% |
| L: L2 | | | |
| *t*: 150 °C | | | |
| **21**, II | $LFe^{III}(O)_2Fe^{III}L^{2+}$ | 342.2 | 100% |
| $[LFe^{III}O(OH)Fe^{III}L](ClO_4)_2$ | $X(CH_3CN)^{3+}$ | 242.2 | 10% |
| ref 3c | $X(CO_2)^{3+}$ | 364.2 | 25% |
| L: L3 | | | |
| *t*: 150 °C | | | |

[a] The formulas indicate the expected connectivity of the dinuclear cation and the expected oxidation state of the metal. The roman numeral after the compound number refers to the core structures in Figure 1. The structure of compounds labeled with an asterisk has been determined by X-ray analysis which together with the preparation is reported in the reference shown. L refers to the ligand using the abbreviations shown in Figure 3. The temperature of the heated capillary (*t*) is listed. [b] X refers to the intact complex cation of the salt shown in the first column. [c] The spectrum of this sample was recorded from a solution in methanol.

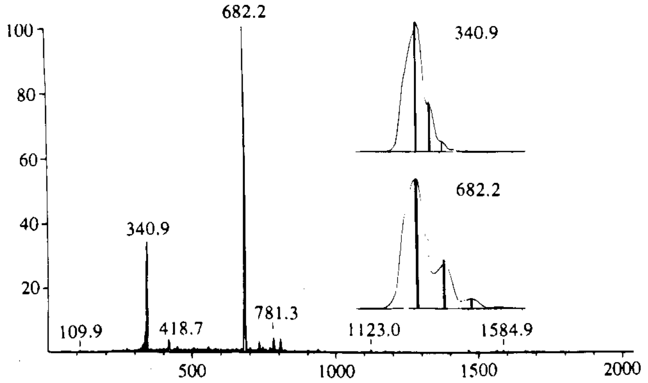

**Figure 3.** ES spectrum of **18**. The spectrum was recorded from a 0.1 mM solution in acetonitrile. The insert show the peaks at *m/z* 340.9 and *m/z* 682.2 in magnification with the calculated isotopic patterns for $[L_2Mn_2O_2]^{2+}$ (*m/z* 340.9) and $[L_2Mn_2O_2]^+$ (*m/z* 682.2) indicated with bars.

along with peaks for the complex cation associated with one and two counteranions are observed (Table 1). The spectrum suggests that this complex is stable in solution and does not rearrange into the dinuclear complex, $[L7Fe^{III}O(CH_3CO_2)_2]^{2+}$.

In a detailed analysis of the data in Table 1 it is important to notice that the efficiency with which the complex ions are transferred from solution into the gas phase is likely to depend on the charge-state of the ions. The lower the number of charges the more efficient this process will be and consequently the relative peak intensities shown in Table 1 are unlikely to be a direct measure of the relative concentrations of the various ions in the sample solution. When, for instance, ions containing additional acetate groups, $[LFe^{III}(CH_3CO_2)]_2O^{2+}$, are observed, *e.g.* in the spectra of **1**, **2**, **4**, and **14** they will have one positive charge fewer than the parent complex and may, as a consequence, appear in relatively greater abundance. The pure ligands (data not shown) give signals that are very much intenser than those due to the complexes and consequently the data in Table 1 indicate that the concentrations of free ligands in the sample solutions must be very low, even in the solution of **7** in whosespectrum the free ligand, **L6**, is the base peak. However, it should be noted that this is a particularly unusual case since the ligand is a quaternary ammonium ion and does not need to be protonated.

Although most of the ES mass spectra summarized in Table 1 can be assigned to the intact complex cations, the ions of the formulation $[LFe^{III}(RCO_2)]_2O^{2+}$ that are observed in the spectra of the carboxylate-bridged complexes, **1**, **2**, **4**, **5**, and **14**, illustrate that these particular complexes are labile in solution and that the ions formed from the solution can be assigned. Assuming that one monodentate acetate ion is coordinated to each iron atom in these ions it seems that once the pure ($\mu_2$-oxo)($\mu_2$-acetato)-bridged diiron(III) complex is dissolved, significant competing equilibria are established. This shows that ES mass spectrometry may prove useful in the identification of some of the species formed in solutions of oxo-bridged complexes, some of which may be intermediates in the formation of higher nuclearity aggregates.

It should be noted that a peak for the intact complex cation is observed in the spectra of all complexes except in that of complex **15**. The crystal structure of **15**, as determined by X-ray analysis,[3a] shows that a molecule of water is coordinated to each iron atom. These aquo ligands are apparently too labile to remain coordinated to iron atoms under the ES conditions. Also, as shown in Table 1, the most abundant peak in the spectrum of **21** is due to the di($\mu_2$-oxo)diiron(III) species. The bridging hydroxide ion of **21** has apparently lost its proton during the desolvation process.

The bis($\mu_2$-*O,O'*-acetato)diferrous complex, **14**,[3c] (**IV**, Figure 1) is included in this study to further illustrate the versatility of ES mass spectrometry. The core of this complex is presumably less robust than those containing the relatively tightly bound M$-\mu_2$-O$-$M unit (M$-\mu$-O bond lengths are usually on the order of 1.8 Å).[3a–d] Additionally, **14** is extremely oxygen-sensitive. The ($\mu_2$-oxo)($\mu_2$-acetato)-bridged diiron(III) complex **1**, can be isolated from solutions of **14** exposed to air.[3c] The ES mass spectrum of **14** (prepared in degassed acetonitrile and recorded immediately after preparation) shows the expected peak for $[L3Fe^{II}(\mu_2\text{-}O,O'\text{-}CH_3CO_2)_2Fe^{II}L3]^{2+}$ together with peaks corresponding to the oxidized derivatives listed in Table 1.

The spectra of the dinuclear manganese complexes[3e] can be rationalized on the basis of their well known redox chemistry. The oxidation of the $Mn^{III}_2$ complex **17** is associated with a change in the core structure, and these adducts are observed in the spectrum. The formulations of these adducts are listed in Table 1. The three oxidation states attainable for the bis($\mu_2$-oxo)dimanganese(III/IV) complex, **19**, previously detected by cyclic voltammetry and later isolation[3f] are clearly observed in the ES mass spectrum of **19**.

The results reported here for relatively simple multiply-charged oxo-bridged complexes, along with a the recent report of the use of ESMS for the characterization of a series of single positively charged basic acetate complexes,[10] clearly demonstrate that electrospray ionization mass spectrometry is a very valuable tool in identification of oxo-bridged complexes and in certain cases it may eliminate the need to resort to time-consuming X-ray crystallography.

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