New Heterobinuclear μ-Oxo-bridged Dimer Complexes: Synthesis, Characterization and Structural Studies

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A systematic method for the preparation of heterobinuclear μ-oxo bridged dimer complexes from the reaction of $(C_{22}H_{22}N_4)Ti{=}O$ with other transition metal complexes is reported.

Homonuclear μ-oxo-bridged metal complexes have been extensively studied and have contributed greatly to our current understanding of metal–metal interactions. However, only recently have systematic attempts to prepare and study heterobinuclear μ-oxo-bridged metal complexes been undertaken. The range of interactions in such complexes would be considerably more varied than in homonuclear analogues. The extent of electronic interaction through the bridging atom in heterobinuclear systems, the equality of sharing of the bridging atom, the nature of the bonding (bond angles and donor–acceptor properties of each of the atoms, etc.) have not been extensively explored. An early report of the solution study between adduct formation between the vanadyl oxygen atom and Ru of $Ru(NH_3)_5H_2O^{2+}$, with the predominate associative interaction is $d_\pi \rightarrow \pi^*$ where the π^* orbitals of V=O are analogues to those of CO [1]. Most recently heterobinuclear μ-oxo Cr–O–Fe porphyrin complexes obtained by the reaction of oxochromium(IV) and Fe(II) porphyrins have been characterized [2].

Our approach to the synthesis of this type of complex has been to start with metal complexes containing a reactive M=O moiety and to react this with a complex of a second metal known to form μ-oxo bridged species. We have deliberately chosen different ligands for the two different metals. This avoids ambiguity arising from structural disorder of the two metals centers which would interfere with the interpretation of X-ray crystallographic results. Also, homonuclear μ-oxo bridged species having different polydentate ligands associated with each metal can be studied.

We report herein a series of heterobinuclear μ-oxo-bridged dimers formed by the reaction of the Ti=O bond $(C_{22}H_{22}N_4)Ti{=}O$ [3] with other Ti complexes and with other oxophilic metal complexes. These include Fe(II), Fe(III), Cr(III), Mn(II), V(III), Sn(IV), and Mo(0) (see Table I). It appears that the Ti=O bond of the $(C_{22}H_{22}N_4)$-Ti=O complex is more reactive than (TPP)Ti=O since the latter does not form similar type adducts. The formation of genuine μ-oxo adducts, as opposed to double salts having identical stoichiometry, was indicated by the visible spectrum, which for the adducts differed from the sum of the two independent reactants. More diagnostic however, are the antisymmetric M–O–M′ stretching frequencies (Table I) which should be compared with the values of the two limiting species, $(C_{22}H_{22}N_4)Ti{=}O$, 930 cm^{-1}, and the homonuclear μ-oxo-dimer, $(C_{22}H_{22}N_4)Ti{-}O{-}Ti(C_{22}H_{22}N_4)^{2+}$ of 820 cm^{-1} [3]. It is not possible on the basis of the IR alone to determine which metal is most strongly bound to the oxygen.

TABLE I. Heteronuclear μ-Oxo-dimer Complexes formed from $(C_{22}H_{22}N_4)Ti{=}O$ with Other Transition Metal Complexes

Starting material	Complex	IR frequency of Ti–O–M (cm^{-1})
	$(C_{22}H_{22}N_4)Ti{=}O$	930
	$[(C_{22}H_{22}N_4)Ti{-}O{-}Ti(C_{22}H_{22}N_4)](BPh_4)_2$	820
	[(salen)Fe–O–Fe(salen)]	820
$Ti(salen)Cl_2$	$[(C_{22}H_{22}N_4)Ti{-}O{-}Ti(salen)](BPh_4)_2$	775
Fe(salen)Cl	$[(C_{22}H_{22}N_4)Ti{-}O{-}Fe(salen)]_2(BPh_4)_2$	866
Fe(salen)	$(C_{22}H_{22}N_4)Ti{-}O{-}Fe(salen)$	842
$Cr(salen)PF_6 \cdot 2H_2O$	$[(C_{22}H_{22}N_4)Ti{-}O{-}Cr(salen)]PF_6$	900
Cr(TPP)Cl	$(C_{22}H_{22}N_4)Ti{-}O{-}Cr(TPP)Cl$	906
Mn(salen)	$(C_{22}H_{22}N_4)Ti{-}O{-}Mn(salen)$	884
V(salen)Cl	$(C_{22}H_{22}N_4)Ti{-}O{-}V(salen)Cl$	896
$Sn(CH_3)_3Cl$	$(C_{22}H_{22}N_4)Ti{-}O{-}Sn(CH_3)_3Cl$	913
$Mo(CO)_6$	$(C_{22}H_{22}N_4)Ti{-}O{-}Mo(CO)_5$	898

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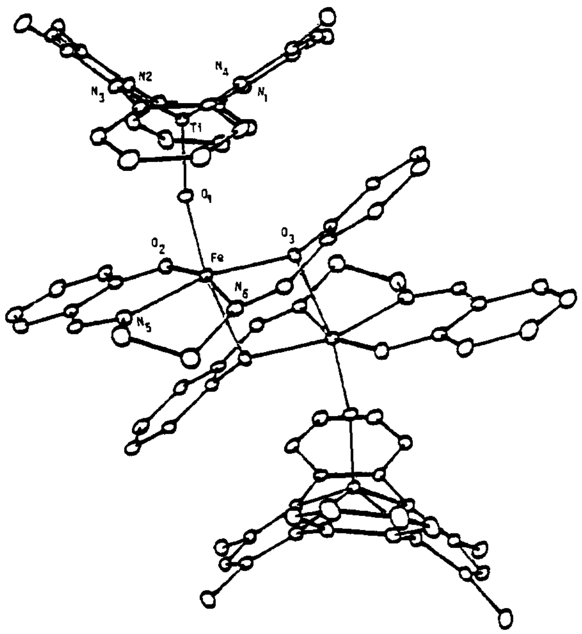

Fig. 1a. Molecular structure of $[(C_{22}H_{22}N_4)Ti{-}O{-}Fe(salen)]_2^{2+}$ cation. Bond parameters within the coordination sphere: Ti–N(ave) = 2.025 (Å), Ti–O(1) = 1.701(6), distance of Ti from N_4 plane = 0.75 Å, Fe–N(5) = 2.104, Fe–N(6) = 2.148, Fe–O(1) = 1.935, Fe–O(2) = 1.909, Fe–O(3) = 2.007, Fe–O(3)(bridge) = 2.178, distance of Fe from N(2)-O(4) plane = 0.14, Ti–O–Fe angle = 161.6°.

As a specific example, the complex formed by the reaction of LTi=O and Fe(salen)Cl* has its Fe–O–Ti antisymmetric absorption at 866 cm^{-1} with no absorptions attributable to Ti=O, Ti–O–Ti, or Fe–O–Fe. The crystal structure of this adduct, $[(C_{22}H_{22}N_4)Ti{-}O{-}Fe(salen)]_2(BPh_4)_2$, was determined to confirm unequivocally the identity of the complex and to provide definitive evidence for the nature of the bridging linkage.** In addition to the expected dimer, further bridging occurred through the iron and salen O atoms to form a tetrameric species (Fig. 1). Of most concern is the Fe–O–Ti linkage, which has a Ti–O distance of 1.701 Å and a Fe–O distance of 1.935 Å with a Fe–O–Ti angle of 161.6° (Table II). The Ti–O distance is lengthened approximately 0.1 Å from the values observed for

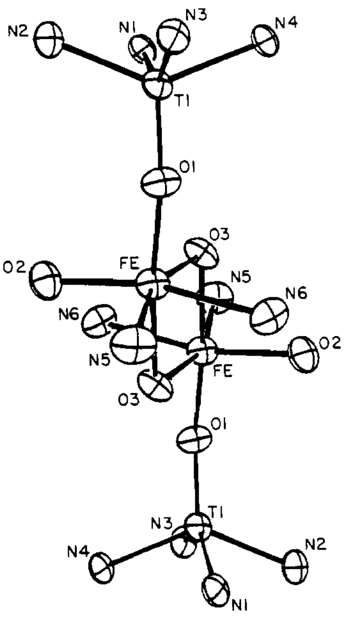

Fig. 1b. ORTEP plot of the coordination spheres of the $[(C_{22}H_{22}N_4)Ti{-}O{-}Fe(salen)]^{2+}$ cation.

TABLE II. Bond Lengths for $[(C_{22}H_{22}N_4)Ti{-}O{-}Fe(salen)]_2(BPh_4)_2$

Atoms	Distance (Å)	Atoms	Distance (Å)
Ti–N(1)	2.012(7)	C(10)–C(11)	1.395(10)
Ti–N(2)	2.040(7)	C(10)–C(15)	1.403(9)
Ti–N(3)	2.016(7)	C(11)–C(12)	1.376(11)
Ti–N(4)	2.033(7)	C(12)–C(13)	1.365(11)
Ti–O(1)	1.701(6)	C(13)–C(14)	1.379(11)
Fe–O(1)	1.935(6)	C(14)–C(15)	1.402(10)
Fe–O(2)	1.909(6)	C(15)–N(4)	1.440(9)
Fe–O(3)	2.178(6)	N(4)–C(16)	1.309(9)
Fe–O(3)	2.007(6)	C(16)–C(16A)	1.530(9)
Fe–N(5)	2.104(8)	C(16)–C(17)	1.393(9)
Fe–N(6)	2.148(8)	C(17)–C(18)	1.406(9)
N(1)–C(1)	1.431(9)	C(18)–C(18A)	1.512(10)
C(1)–C(2)	1.416(10)	C(18)–N(1)	1.317(9)
C(2)–C(3)	1.367(11)	O(2)–C(19)	1.308(9)
C(3)–C(4)	1.369(11)	C(19)–C(20)	1.410(10)
C(4)–C(5)	1.393(11)	C(20)–C(21)	1.355(11)
C(5)–C(6)	1.398(10)	C(21)–C(22)	1.381(12)
C(6)–C(1)	1.385(9)	C(22)–C(23)	1.350(12)
C(6)–N(2)	1.432(9)	C(23)–C(24)	1.398(11)
N(2)–C(7)	1.334(9)	C(24)–C(26)	1.455(10)
C(7)–C(7A)	1.506(10)	C(26)–N(5)	1.306(10)
C(7)–C(8)	1.420(9)	N(5)–C(27)	1.489(11)
C(8)–C(9)	1.389(9)	C(27)–C(28)	1.523(11)
C(9)–C(9A)	1.522(11)	C(28)–N(6)	1.491(11)
C(9)–N(3)	1.309(9)	N(6)–C(29)	1.280(10)
N(3)–C(10)	1.436(9)	N(6)–C(29)	1.280(10)
C(29)–C(30)	1.436(10)	C(30)–C(31)	1.420(10)
C(31)–C(32)	1.380(10)	C(32)–C(33)	1.424(11)

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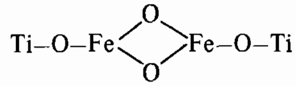
*salen = N,N'-bis(salicylideneiminato) ligand.

**Crystallographic data: Crystals of $[(C_{22}H_{22}N_4)Ti{-}O{-}Fe(salen)]_2(BPh_4)_2$ were dark brown, triclinic, space group $P\bar{1}$, with a = 13.122(4), b = 13.883(12), c = 14.539(5) Å, α = 94.21(5), β = 93.08(3), γ = 99.46°, Z = 2, U = 2600(4). The structure was solved and refined from 4973 independent reflections with $2 < 2\theta(\text{Mo K}\alpha) < 50°$ and $I > 2\sigma(I)$ from a total of 9196 reflections collected. At convergence, R_1 = 8.2, R_2 = 9.3, for anisotropic thermal vibration parameter for metal atoms of the ligands, isotropic thermal parameters for the B and carbon atoms of BPh_4^- anions and fixed contributions for hydrogen atoms.

TABLE II. *(continued)*

Atoms	Distance (A)	Atoms	Distance (A)
C(33)–C(34)	1.418(10)	C(34)–C(35)	1.406(9)
C(35)–O(3)	1.362(9)	B–C(36)	1.644(11)
B–C(42)	1.671(11)	B–C(48)	1.642(11)
B–C(54)	1.633(11)	C(36)–C(37)	1.422(10)
C(37)–C(38)	1.445(10)	C(38)–C(39)	1.372(10)
C(39)–C(40)	1.419(10)	C(40)–C(41)	1.433(10)
C(41)–C(36)	1.420(10)	C(42)–C(43)	1.421(9)
C(43)–C(44)	1.404(10)	C(44)–C(45)	1.410(10)
C(45)–C(46)	1.367(10)	C(46)–C(47)	1.389(10)
C(47)–C(42)	1.446(10)	C(48)–C(49)	1.389(12)
C(49)–C(50)	1.467(12)	C(50)–C(51)	1.387(13)
C(51)–C(52)	1.315(12)	C(52)–C(53)	1.422(12)
C(53)–C(48)	1.400(10)	C(54)–C(55)	1.404(10)
C(55)–C(56)	1.394(11)	C(56)–C(57)	1.428(12)
C(57)–C(58)	1.407(13)	C(58)–C(59)	1.420(13)
C(59)–C(54)	1.433(11)		

the Ti–O complexes of phthalocyanine, 1.650(4), (monoclinic form), 1.626(7) (triclinic form) [4], and porphyrin, 1.613(5) Å [5] respectively. It is shorter than in the Ti–O–Ti linkage (1.838) of [($N_4C_{12}H_{25}$)] and other Ti–O–Ti complexes [6]. The Fe–O distance is approximately 0.1 Å longer than observed in several [(Fe(salen)]$_2$O structural determinations [7]. The Fe–O–Ti angle is larger than the μ-oxo Fe(salen) complex, ~140°, and the almost linear Ti–O–Ti angle 152.0 [6].

Apparently, as a result of the reduced Fe–O bonding interaction, dimerization of the Fe(salen) moieties occurs, via weak Fe–O bridging [7] interactions, 2.178 Å, from the Fe of one unit through the salen O atom of an adjacent Fe(salen) complex occurs through a crystallographic inversion center. This leads to an unusual four atom,  tetrameric unit. Similar dimerization has been observed in one of the crystalline forms of Fe(salen)Cl [8]. As a consequence of this bridging interaction, the six coordinate iron is displaced only nominally, 0.14 Å, from the N_2O_2 salen donor atom plane, compared to the 0.5 Å displacements observed in the [Fe(salen)$_2$]O structures.

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