Inorg. Chem. **1988**, *27*, 593–594

A New Class of Bis(μ-aryloxy)-Bridged Dimers with First-Row Divalent Transition-Metal Ions. Synthesis and Structural Characterization of the $(Et_4N)_2[M_2Cl_4(O\text{-}C_6H_4\text{-}p\text{-}CH_3)_2]$ Complexes (M = Mn(II), Fe(II), Co(II), Zn(II), and Cd(II))

Sir:

The coordination chemistry of first-row transition-element μ_2 dimers with simple aryloxide bridging ligands is virtually unexplored. In contrast, numerous dimeric complexes that contain the $[(\mu\text{-OAr})_2M_2]$ centers are known mainly with the tetradentate *N,N'*-ethylenebis(salicylideneaminato) ligand (SALEN) and its derivatives. Among these complexes are included the structurally characterized $[Cu(SALEN)]_2$,[1] $[Fe(SALEN)Cl]_2$,[2] $[Co(SALEN)X]_2$,[3] and the recently reported $[Mn(SALPS)]_2$.[4] Interest in complexes that contain the $[(\mu\text{-OAr})_2M_2]$ units derives in part from their basic importance in the study of intermetallic magnetic and hyperfine interactions. Such studies are needed for a detailed understanding of similar interactions associated with the M–O–M dimeric units in certain metalloproteins such as hemerythrin[5] and ribonucleotide reductase[6] (M = Fe^{3+}) and possibly in the manganese pseudocatalase enzyme of *Lactobacillus plantarum*[7] (M = Mn^{3+}) and the polynuclear manganese centers present in photosynthetic enzymes.[8]

The crystalline $(Et_4N)_2[M_2Cl_4(O\text{-}C_6H_4\text{-}p\text{-}CH_3)_2]$ complexes (M = Mn (I), Fe (II), Co (III), Zn (IV), and Cd (V)) are obtained[9] readily by the anaerobic reaction of equimolar amounts of Et_4NCl, $NaOC_6H_4\text{-}p\text{-}CH_3$, and the appropriate anhydrous, bivalent metal chlorides in refluxing, dry CH_3CN. Single crystals of pale pink I, white II, dark blue III, and white IV and V can be obtained by slow cooling of hot concentrated CH_3CN solutions of these compounds. The crystalline compounds are X-ray isomorphous and isostructural.[10] The centrosymmetric $[M_2Cl_4(O\text{-}C_6H_4\text{-}p\text{-}CH_3)_2]^{2-}$ anions (Figure 1) can be described in terms of two edge-sharing tetrahedral units with each of the divalent ions coordinated by two terminal chlorides and the two bridging *p*-cresolate ligands. The M–M repulsions appear to dominate the structure of the M_2O_2 rhombic units that are elongated by the M–X–M criterion.[11] Thus, the M–O–M angles in all structures are ~30° larger than the idealized value of 70.5°[11] and range from 99.7 (1) to 103.0 (2)°. A deviation of similar magnitude also is found in the O–M–O angles. The latter (range 77.0 (2)–80.3 (1)°) are ~30° smaller than the idealized value of 109.5°. The intradimer distances between the *p*-cresolate oxygen atoms are rather short and range from 2.533 (12) Å in II to 2.749 (6) Å in V. The bridging oxygen atoms are planar, and the plane of the two phenyl rings is rotated relative to that of the M_2O_2 rhombic unit by ~15°.

The magnetic moments of I, II, and III (μ_{eff}^{cor}, 300 K) at 5.34, 4.80, and 4.48 μ_B, respectively, are smaller than the values expected for monomeric tetrahedral complexes and suggest that the metal ions in the dimers are weakly coupled. A study of the magnetic

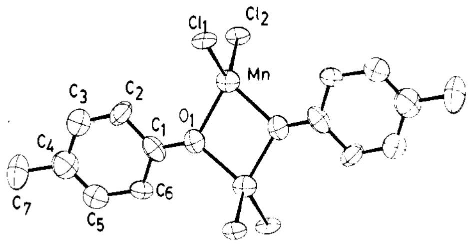

Figure 1. Structure and labeling of the $[Mn_2Cl_4(O\text{-}C_6H_4\text{-}p\text{-}CH_3)_2]^{2-}$ anion. The structures and labeling of II–V are exactly analogous. Thermal ellipsoids as drawn by ORTEP[17] represent the 50% probability surfaces.

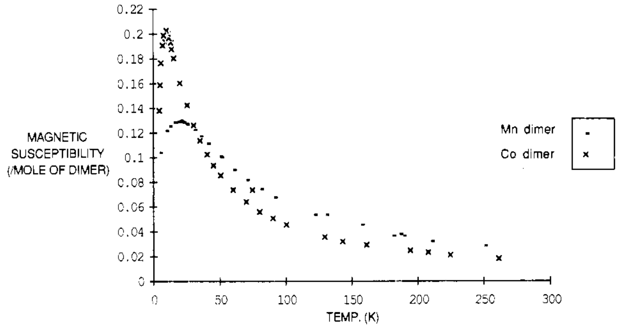

Figure 2. Magnetic susceptibility (χ) vs temperature (K) data for the $(Et_4N)_2[M_2Cl_4(O\text{-}C_6H_4\text{-}p\text{-}CH_3)_2]$ complexes (data points are plotted as × and – for M = Co and Mn, respectively).

Table I. Selected Structural Parameters in the $[Cl_2M(\mu\text{-}p\text{-}CH_3\text{-}C_6H_4O)]_2^{2-}$ Anions (M = Mn, Fe, Co, Zn, Cd)

	Mn	Fe	Co	Zn	Cd
			Distances (Å)		
M–M	3.186 (1)	3.177 (3)	3.034 (1)	3.057 (1)	3.456 (1)
M–O	2.070 (2)	2.021 (5)	1.985 (3)	1.998 (3)	2.209 (3)
M–O′	2.074 (2)	2.042 (5)	1.983 (3)	1.987 (3)	2.207 (3)
M–Cl(1)	2.315 (1)	2.247 (3)	2.227 (1)	2.217 (1)	2.390 (1)
M–Cl(2)	2.320 (1)	2.251 (3)	2.233 (1)	2.218 (1)	2.397 (1)
O–O′	2.649 (3)	2.533 (12)	2.558 (5)	2.557 (6)	2.749 (6)
O–C	1.352 (4)	1.368 (9)	1.347 (5)	1.358 (5)	1.334 (5)
			Angles (deg)		
O–M–O′	79.5 (1)	77.1 (2)	80.3 (1)	79.8 (1)	77.0 (2)
M–O–M	100.5 (2)	102.9 (2)	99.7 (1)	100.2 (1)	103.0 (2)
M–O–C	130.6 (2)	130.6 (5)	129.4 (2)	128.7 (3)	127.6 (3)
M–O′–C′	128.9 (2)	126.6 (5)	130.9 (2)	131.1 (3)	129.3 (3)
Cl–M–Cl	116.5 (1)	116.3 (1)	113.3 (1)	115.4 (1)	119.7 (1)
Cl(1)–M–O	114.3 (1)	114.2 (2)	115.5 (1)	114.9 (1)	113.9 (1)
Cl(2)–M–O	114.0 (1)	114.9 (2)	113.7 (1)	113.1 (1)	111.7 (1)
Cl(1)–M–O′	114.2 (1)	115.3 (2)	115.2 (1)	114.4 (1)	114.2 (1)
Cl(2)–M–O′	112.9 (1)	113.2 (2)	115.0 (1)	114.2 (1)	112.7 (1)

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(9) After recrystallization the yields for I, II, III, IV, and V were 73%, 46%, 44%, 37%, and 61%, respectively. The crystalline products show essentially identical powder patterns. The calculated powder pattern for one of these (2θ values, (Cu Kα) = 1.5418 Å, I, the first 14 lines), with the relative intensities normalized to 100 is as follows: 9.446 (54.4), 10.049 (100.0), 11.079 (65.4), 12.122 (33.6), 12.405 (35.7), 14.577 (19.0), 15.139 (14.7), 16.726 (21.2), 17.293 (35.3), 17.916 (45.4), 18.974 (58.9), 19.913 (62.9), 21.530 (47.5), 22.879 (19.8) Å. Observed: 9.42 (m), 10.05 (vs), 11.05 (s), 12.10 (m), 12.43 (m), 14.55 (w), 15.23 (w), 16.73 (w), 17.28 (m), 17.95 (m), 19.00 (s), 19.93 (s), 21.52 (s), 22.90 (w) Å.

(10) Crystal and refinement data: for I, a = 11.712 (2) Å, b = 10.938 (4) Å, c = 14.650 (2) Å, β = 92.94 (1)°; for II, a = 11.632 (6) Å, b = 10.903 (5) Å, c = 14.578 (7) Å, β = 93.27 (4)°; for III, a = 11.538 (3) Å, b = 10.951 (2) Å, c = 14.528 (2) Å, β = 92.90 (2)°; for IV, a = 11.564 (2) Å, b = 11.011 (2) Å, c = 14.539 (4) Å, β = 92.75 (2)°; for V, a = 11.902 (3) Å, b = 10.882 (3) Å, c = 14.728 (3) Å, β = 93.77 (2)°; for I, d_{calcd} = 1.29 g/cm^3, d_{obsd} = 1.27 (1) g/cm^3, μ = 9.2 cm^{-1}, $2\theta_{max}$ = 40 (λ(Mo Kα) = 0.710 69 Å), 1770 unique reflections, 1372 used in refinement ($F_o^2 > 3\sigma(F_o^2)$), 181 variable parameters, final R = 0.030; for II, d_{calcd} = 1.31 g/cm^3, d_{obsd} = 1.32 (1) g/cm^3, μ = 10.6 cm^{-1}, $2\theta_{max}$ = 40° (λ(Mo Kα) = 0.710 69 Å), 1739 unique reflections, 1210 used in refinement ($F_o^2 > 3\sigma(F_o^2)$), 181 variable parameters, final R = 0.046; for III, d_{calcd} = 1.33 g/cm^3, d_{obsd} = 1.32 (1) g/cm^3, μ = 11.8 cm^{-1}, $2\theta_{max}$ = 40° (λ(Mo kα) = 0.710 69 Å), 1533 unique reflections, 1387 used in refinement ($F_o^2 > 3\sigma(F_o^2)$), 181 variable parameters, final R = 0.030; for IV, d_{calcd} = 1.34 g/cm^3, d_{obsd} = 1.32 (1) g/cm^3, μ = 16.05 cm^{-1}, $2\theta_{max}$ = 40° (λ(Mo Kα) = 0.710 69 Å), 1737 unique reflections, 1335 used in refinement ($F_o^2 > 3\sigma(F_o^2)$), 181 variable parameters, final R = 0.030; for V, d_{calcd} = 1.47 g/cm^3, d_{obsd} = 1.45 (1) g/cm^3, μ = 13.82 cm^{-1}, $2\theta_{max}$ = 40° (λ(Mo Kα) = 0.710 69 Å), 1606 unique reflections, 1506 used in refinement ($F_o^2 > 3\sigma(F_o^2)$), 181 variable parameters, final R = 0.024.

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susceptibility vs temperature from 1.8 to 250 K shows (Figure 2) typical antiferromagnetic behavior for I and III with maxima at ~19 and ~9 K. A preliminary fit of the magnetic data for I has been obtained by using a derived[12] equation based on the Heisenberg model for spin–spin interactions ($E(S) = -JS_1S_2$) in a coupled $S = {}^5/_2/S = {}^5/_2$ system. The derived coupling constant J is -5.0 cm^{-1} for $g = 2.00$. A satisfactory fit could not be obtained by using the same model for III, presumably due to the single-ion anisotropy for a Co(II) ion. However, the temperature dependence of the magnetic susceptibility suggests that J is between 0 and -10 cm^{-1}. A maximum in the χ vs T curve for II was not found within the temperature range studied. The lack of significant magnetic coupling, suggested by the magnetic studies, also is apparent in the ^{57}Fe Mössbauer spectrum of II. The spectrum at 4.2 K in an applied magnetic field of 7.8 kG indicates very weak coupling (if any at all!) between the two irons. The zero-field spectrum at 4.2 K shows a sharp doublet with an isomer shift of 1.00 (1) mm/s (vs Fe at room temperature) and a quadrupole splitting of 2.40 (1) mm/s. The IS value is similar to the one reported[13] for the $(FeCl_4)^{2-}$ complex (1.01 mm/s).[14]

The EPR spectrum of I in DMF solution shows a six-line spectrum with a nuclear hyperfine splitting of 81.6 G and indicates that the dimer undergoes solvolysis and dissociates to a monomeric Mn(II) species. This dissociation very likely occurs in coordinating solvents with the other members of the $[M_2Cl_4(O\text{-}C_6H_4\text{-}p\text{-}CH_3)_2]$ series as well and should be taken into account in the evaluation of the solution properties of these compounds. Cyclic voltammetric studies in CH_3CN solution show irreversible oxidation waves for I and III and a reversible wave for II ($E_{1/2} = +0.08$ V vs SCE). The solvolytic dissociation of the dimers in donor solvents makes it difficult to identify the exact nature of the electroactive species in solutions of II. The electronic spectrum of III in CH_3CN solution is typical of tetrahedrally coordinated Co(II) with transitions at 658 (sh), 644, 630 (sh), 560, 534 (sh), 360 (sh), and 278 nm.

The $[M_2Cl_4(O\text{-}C_6H_4\text{-}p\text{-}CH_3)_2]^{2-}$ anions are ideally suited as reagents for the synthesis of other dinuclear complexes by substitution of the chloride ligands in metathetical reactions. This synthetic utility already has been demonstrated in reactions of the $[M_2Cl_4(O\text{-}C_6H_4\text{-}p\text{-}CH_3)_2]^{2-}$ dimers with $AgNO_3$ and the formation of the $[M_2(NO_3)_4(O\text{-}C_6H_4\text{-}p\text{-}CH_3)_2]^{2-}$ dimers[16] (M = Mn, Co). The structures of these new dimers have been determined and show $[M_2(O\text{-}C_6H_4\text{-}p\text{-}CH_3)_2]^{2+}$ cores very similar to those in the chloro analogues.

Acknowledgment. The support of this work by a grant (GM 26671) from the National Institutes of Health is gratefully acknowledged.

Supplementary Material Available: Tables SI and SII, listing positional and thermal parameters of all atoms in the asymmetric unit of $(Et_4N)_2[Mn_2Cl_4(O\text{-}C_6H_4\text{-}p\text{-}CH_3)_2]$ (4 pages); a table of calculated and observed structure factors (6 pages). Ordering information is given on any current masthead page.

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Photoreactions of $Ir_8(CO)_{22}{}^{2-}$. Homolytic Cleavage of an Unsupported Metal–Metal Bond Linking Two Tetrahedral Iridium Carbonyl Clusters

Sir:

The photoreactions of dinuclear metal complexes linked by a metal–metal single bond have been subject to considerable attention over the past decade.[1–6] An example is $Mn_2(CO)_{10}$ for which photolysis leads to competitive reactions: homolytic cleavage of the metal–metal bond and dissociation of CO.[1,7] The former, which results from excitation of $\sigma_{MM} \rightarrow \sigma^*_{MM}$ and/or $\pi_{ML} \rightarrow \sigma^*_{MM}$ transitions, gives mononuclear 17-electron metal radical intermediates, i.e.

$$L_xM\text{-}ML_x \xrightarrow{h\nu} 2L_xM^\bullet \qquad (1)$$

Described here is a previously unexplored elaboration of this theme to a case where the metal–metal bond photolyzed links two polyhedral metal clusters. The specific example is the octairidium anion $Ir_8(CO)_{22}{}^{2-}$, which consists of two $Ir_4(CO)_{11}{}^-$ tetrahedra linked by a metal–metal single bond unsupported by bridging ligands.[8] It is shown here that photolysis of this remarkable polynuclear species apparently leads to homolytic bond cleavage to give the reactive cluster radical anion $Ir_4(CO)_{11}{}^-$.

The electronic spectrum of the PPN$^+$ salt (PPN$^+$ = N$(PPh_3)_2{}^+$)[9] of $Ir_8(CO)_{22}{}^{2-}$ in methylene chloride solution displays an intense absorption band at 532 nm ($\epsilon = 1.68 \times 10^4$ M^{-1} cm^{-1}, Figure 1). Since no visible range bands are apparent in the electronic spectra of the tetrahedral clusters $Ir_4(CO)_{12}$ or $HIr_4(CO)_{11}{}^-$,[10,11] we have assigned this band as a $\sigma_{MM} \rightarrow \sigma^*_{MM}$ orbital transition localized to the bond linking the two clusters in analogy to the strong $\sigma_{MM} \rightarrow \sigma^*_{MM}$ absorption bands of dinuclear complexes such as $Mn_2(CO)_{10}$ and $[(\eta^5\text{-}C_5H_5)W(CO)_3]_2$.[1,12]

Solutions of $[PPN]_2[Ir_8(CO)_{22}]$ under CO in various solvents were observed to be indefinitely stable in the dark; however, exposure even to ambient room light resulted in rapid conversion to yellow solutions. The product of quantitative 520 nm photolysis in dichloromethane solution under N_2 (Figure 1) was shown to be the chlorotetrairidium anion $Ir_4(Cl)(CO)_{11}{}^-$ by comparing the IR and UV–vis spectra to those of an authentic sample[13] under identical conditions. Analogous 520-nm photolysis in CH_2Cl_2

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