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Synthesis, Structure and Cation-Binding Properties of Some [4 + 4] Metallocyclic MO_2^{2+} (M = Mo or W) Derivatives of 9-Phenyl-2,3,7-trihydroxyfluor-6-one

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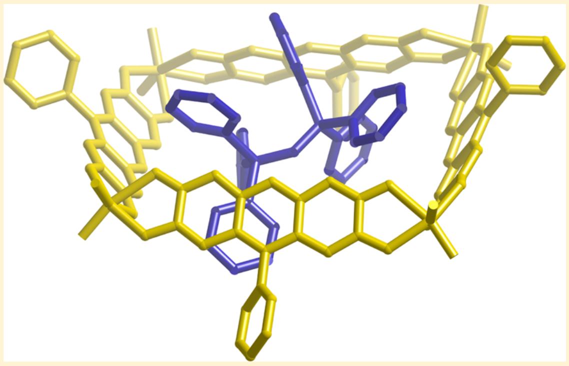
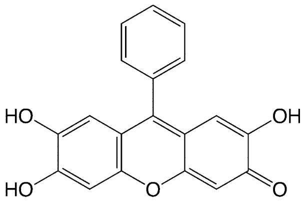
Supporting Information



ABSTRACT: The trianion Z^{3-} obtained from 9-phenyl 2,3,7-trihydroxyfluor-6-one, ZH_3, affords dioxomolybdenum and dioxotungsten derivatives which contain [4 + 4] metallocycles of composition $[(MO_2)_4Z_4]^{4-}$ (M = Mo, W) in combination with a variety of counter cations. The syntheses, structures and ESMS of the following compounds are presented: compound **1**, $(MePPh_3)_3(NBu_4)[(MoO_2)_4Z_4]$; compound **2**, $(MePPh_3)_3(NBu_4)[(WO_2)_4Z_4]$; compound **3**, $(MePPh_3)_4[(WO_2)_4Z_4]$; compound **4**, $(PPh_4)_2(NBu_4)_2[(MoO_2)_4Z_4]$; compound **5**, $(AsPh_4)_3(NBu_4)[(MoO_2)_4Z_4]$; compound **6**, $(AsPh_4)_2(NBu_4)_2[(WO_2)_4Z_4]$; compound **7**, $(Ph_3PNPPh_3)(NBu_4)_3[(MoO_2)_4Z_4]$; compound **8**, $(Ph_3PNPPh_3)(NBu_4)_3[(WO_2)_4Z_4]$; compound **9**, $(NEt_4)(NBu_4)_3[(MoO_2)_4Z_4]$. The metallocycles in all of these compounds have similar structures, with the four metal centers located at the corners of a square slightly distorted, to varying degrees, toward a rhombus and also toward a tetrahedron. Various cations are bound inside the anionic metallocycles. ESI mass spectrometry shows that the metallocycles remain intact in the gas phase, forming $[(MO_2)_4Z_4]^{4-}$, $\{X\text{-}[(MO_2)_4Z_4]\}^{3-}$ and in some cases $\{X_2\text{-}[(MO_2)_4Z_4]\}^{2-}$ where X^+ is an organic cation.

INTRODUCTION

9-Substituted 2,3,7-trihydroxyfluor-6-ones have been known for over a century[1] and have been much used in the spectrophotometric determination of various metals.[2] The results presented here are concerned with the 9-phenyl derivative, **I** (hereafter ZH_3). The synthesis and redox properties of a number of Z^{3-}-bridged binuclear complexes have been explored, and interestingly, a Ni_2 complex in which the bridge has been oxidized to the $Z^{2-\bullet}$ radical state can be isolated.[3] Prior to the recent report of the X-ray crystal structures of $(ZH_4)(HSO_4)$, ZH_3, $(EtPr_2NH)(ZH_2)$, $(PPh_4)(ZH_2)$ and K_3Z,[4] only three crystallographic studies of such 9-substituted 2,3,7-trihydroxyfluor-6-ones had been published, viz., those of $[Ru_2(PPh_3)_4(CO)_4Z](PF_6)$[3d] and metal-free derivatives in which the 9-substituent is an *o*-benzenesulfonic acid group[5] or a *p*-methoxycarbonylphenyl group.[6] The trianion has a number of features which makes it a potentially useful ligand for linking metal centers in oligomeric and polymeric systems. First, the charged chelating groups are expected to provide strong connections to metal centers, and thus it would be expected to promote the formation of robust coordination networks. Second, as indicated above, the ligand is capable of undergoing oxidation thus offering the prospect of generating discrete or polymeric redox-active frameworks. Finally, the relatively long length of the ligand means that metal centers would be separated by distances approaching 13 Å, and thus it is reasonable to expect the formation of large intraframework voids upon assembly of a network.



I

In our initial exploration of metal−ligand assemblies involving Z^{3-} we directed our attention to the formation of simple metallocycles. The *cis*-$M^{VI}O_2^{2+}$ (M = Mo, W) unit has been shown to serve as an "elbow" connector in [2 + 2] and [3 + 3] metallocycles[7] involving bis-catecholate ligands, and we anticipated that such a unit may play a similar geometric role in the generation of metallocycles involving Z^{3-}. This report describes the synthesis and characterization of a number of compounds containing [4 + 4] metallocycles of composition $[(MO_2)_4Z_4]^{4-}$ (M = Mo, W) in combination with a variety of counter cations.

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Table 1. Crystal Data and Refinement Details for Compounds 1−9

	1·6MeOH·0.5H_2O	**2**·3MeOH·3.5H_2O	**3**·5.5MeOH·2.5H_2O	**4**·5.5MeOH·2H_2O	**5**·6MeOH
formula	$C_{155}H_{151}Mo_4NO_{34.5}P_3$	$C_{152}H_{145}NO_{34.5}P_3W_4$	$C_{157.5}H_{135}O_{36}P_4W_4$	$C_{161.5}H_{174}Mo_4N_2O_{35.5}P_2$	$C_{170}H_{156}As_3Mo_4NO_{34}$
M_r	3056.44	3366.00	3462.94	3156.73	3365.48
cryst syst	triclinic	triclinic	triclinic	triclinic	triclinic
space group	$P\bar{1}$	$P\bar{1}$	$P\bar{1}$	$P\bar{1}$	$P\bar{1}$
a/Å	14.7748(3)	14.7533(11)	14.7679(7)	18.8382(12)	18.8066(4)
b/Å	21.8810(5)	21.844(2)	22.1004(11)	20.1833(14)	21.1275(4)
c/Å	24.4420(5)	24.536(2)	24.4164(11)	22.397(2)	21.7979(5)
α/deg	73.209(2)	73.335(1)	72.927(4)	87.328(1)	90.180(2)
β/deg	82.452(2)	81.164(2)	82.588(4)	88.310(1)	109.883(2)
γ/deg	87.043(2)	86.668(1)	87.114(4)	66.960(1)	92.257(2)
V/Å^3	7498.6(3)	7484.2(9)	7553.5(6)	7827.5(9)	8137.2(3)
Z	2	2	2	2	2
μ/mm^{-1}	3.594	3.170	6.511	0.408	3.740
unique reflns	28126	25996	26850	27225	30364
R_{int}	0.0315	0.0299	0.0581	0.0545	0.0409
reflns ($I > 2\sigma(I)$)	17835	18115	17770	15164	18600
Flack param					
$wR2$ (all data)	0.2413	0.2204	0.3514	0.2276	0.2664
R_1 ($I > 2\sigma(I)$)	0.0712	0.0739	0.1181	0.0791	0.0872

	6·3MeOH·H_2O	**7**·4.5MeOH·H_2O	**8**·0.5MeOH·0.5H_2O	**9**·7.75MeOH·0.25H_2O
formula	$C_{159}H_{163}As_2N_2O_{32.50}W_4$	$C_{164.5}H_{194}Mo_4N_4O_{33.5}P_2$	$C_{160.5}H_{177}N_4O_{29}P_2W_4$	$C_{139.75}H_{195.5}Mo_4N_4O_{36}$
M_r	3507.15	3208.94	3423.40	2755.08
cryst syst	triclinic	triclinic	triclinic	monoclinic
space group	$P\bar{1}$	$P\bar{1}$	$P\bar{1}$	$C2$
a/Å	18.4245(5)	18.9580(3)	18.4066(4)	26.8568(4)
b/Å	20.6396(7)	21.1324(6)	20.8649(2)	30.8169(4)
c/Å	21.9240(8)	22.6782(4)	21.3598(5)	17.4524(3)
α/deg	85.629(3)	75.049(2)	88.312(1)	90
β/deg	85.911(3)	82.216(2)	65.145(2)	94.508(2)
γ/deg	65.710(3)	63.834(2)	83.726(1)	90
V/Å^3	7569.7(4)	7875.9(3)	7397.6(2)	14399.7(4)
Z	2	2	2	4
μ/mm^{-1}	6.563	3.351	6.408	3.409
unique reflns	26735	27709	25897	22080
R_{int}	0.0972	0.0391	0.0282	0.0350
refls ($I > 2\sigma(I)$)	12651	18563	19549	16831
Flack param				0.075(13)
$wR2$ (all data)	0.2348	0.1641	0.1964	0.2517
R_1 ($I > 2\sigma(I)$)	0.0817	0.0591	0.0612	0.0812

■ EXPERIMENTAL SECTION

Synthesis. Preparation of (NBu_4)(ZH_2). Hünig's base (6.00 mL, 34.5 mmol) was added to a boiling solution of ZH_3 (2.55 g, 7.96 mmol) and NBu_4Br (5.36 g, 16.6 mmol) in a minimum volume of *N*,*N*-dimethylformamide (~40 mL). The bright orange solution was converted from a bright orange color to a deep purple. The solution was allowed to boil for 10 min before cooling slowly to room temperature. Dark red crystals with green iridescence formed upon cooling. Yield: 4.07 g (91%). Elemental anal. (%), found: C, 75.08; H, 8.65; N, 2.59. Calcd for (NBu_4)(H_2Z) ($C_{35}H_{47}NO_5$): C, 74.83; H, 8.43; N, 2.49. ^{1}H NMR (400 MHz, DMSO-d_6, rt) δH: 0.27 (t, 12H, −CH_3), 0.64 (m, 8H, −CH_2CH_3), 0.90 (m, 8H, −CH_2−), 1.84 (m, 8H, N−CH_2−), 5.41 (s, 2H, C−H), 5.59 (s, 2H, C−H), 6.70 (m, 2H, Ar), 6.94 (m, 3H, Ar). ^{13}C NMR (100.5 MHz, DMSO-d_6, rt) δC: 13.72 (−CH_3), 19.24 (−CH_2CH_3), 23.08 (−CH_2−), 57.54 (N−CH_2−), 99.12, 100.08, 101.84, 102.71, 108.52, 127.97, 128.56, 128.98, 135.15, 147.30, 148.8, 154.27, 170.98 (C=O).

($PMePh_3$)$_3$(NBu_4)[(MoO_2)$_4Z_4$] (1). An aqueous solution (1 mL) of $Na_2MoO_4·2H_2O$ (42 mg, 0.17 mmol) was added to a solution of (NBu_4)(ZH_2) (100 mg, 0.18 mmol), NBu_4Br (172 mg, 0.53 mmol) and $PMePh_3Br$ (195 mg, 0.55 mmol) in methanol (24 mL). The deep red solution was then acidified with glacial acetic acid (2 drops), and deep red amorphous precipitate formed. Upon standing for several days, deep red needle-shaped crystals with green iridescence formed amid the amorphous precipitate, which was almost completely converted to needle crystals over a period of several months. The crystals were collected, washed with methanol and dried in air. Crystallographic analyses on this compound, in addition to the other metallocycle compounds reported, indicate that the crystals form as a solvate containing both methanol and water. Upon exposure to the atmosphere the crystals lose methanol and absorb water. The elemental analyses on this compound as well as the other metallocycles described below correspond to hydrated forms. Yield: 46 mg (36%). IR (KBr) ν cm^{-1}: 3436, 2960, 1619, 1482, 1372, 1313, 1225, 1178, 956, 919, 744, 718, 702, 657, 599, 463. UV−vis λ (nm): 526 (max), 554. Elemental anal. (%), found: C, 60.14; H, 4.63; N, 0.63. Calcd for ($PMePh_3$)$_3$(NBu_4)-[(MoO_2)$_4Z_4$]·6H_2O ($C_{149}H_{138}Mo_4NO_{34}P_3$): C, 60.39; H, 4.69; N, 0.47.

($PMePh_3$)$_3$(NBu_4)[(WO_2)$_4Z_4$] (2). An aqueous solution (1 mL) of $Na_2WO_4·2H_2O$ (59 mg, 0.18 mmol) was added to a solution of (NBu_4)(ZH_2) (100 mg, 0.18 mmol) and $PMePh_3Cl$ (280 mg, 0.90 mmol) in methanol (24 mL). The deep red solution was then acidified using glacial acetic acid (2 drops) to form a bright orange amorphous precipitate. Bright red crystals with green iridescence formed amid the orange precipitate after standing at room temperature for several days.

The crystals were separated from the amorphous solid by agitating the solution, allowing the crystals to settle and decanting off the supernatant liquid and amorphous solid. If necessary, the mother liquor was replaced with methanol and the process repeated until the crystals were completely isolated. Unless otherwise stated, this method of separating crystals from the amorphous precipitate was used in all of the syntheses described below. The crystals were collected, washed with methanol and dried in air. Yield: 19 mg (13%). IR (KBr) ν cm^{-1}: 3436, 2960, 1482, 1374, 1311, 1224, 1178, 936, 891, 744, 662, 601, 465. UV−vis λ (nm): 510 (max), 534. Elemental anal. (%), found: C, 53.37; H, 3.94; N, 0.40. Calcd for $(PMePh_3)_3(NBu_4)[(WO_2)_4Z_4]\cdot 8H_2O$ ($C_{149}H_{142}NO_{36}P_3W_4$): C, 53.41; H, 4.27; N, 0.42.

$(PMePh_3)_4[(WO_2)_4Z_4]$ (3). An aqueous solution (0.5 mL) of $Na_2WO_4\cdot 2H_2O$ (29 mg, 0.088 mmol) was added to a suspension of ZH_3 (29 mg, 0.091 mmol) in a methanolic solution (15 mL) of $PMePh_3Br$ (127 mg, 0.36 mmol). The orange suspended solid changed to a red color, and the reaction mixture was acidified using glacial acetic acid (1 drop). Bright red crystals with green iridescence formed amid the amorphous solid upon standing of the reaction mixture for several days. The crystals were collected, washed with ethanol and dried in air. Yield: 40 mg (56%). IR (KBr) ν cm^{-1}: 1622, 1588, 1483, 1374, 1310, 1222, 956, 932, 885, 745, 663, 602, 464. Elemental anal. (%), found: C, 54.13; H, 3.48. Calcd for $(PMePh_3)_4[(WO_2)_4Z_4]\cdot 7H_2O$ ($C_{140}H_{122}O_{35}P_4W_4$): C, 54.21; H, 3.65.

$(PPh_4)_2(NBu_4)_2[(MoO_2)_4Z_4]$ (4). An aqueous solution (1 mL) of $Na_2MoO_4\cdot 2H_2O$ (43 mg, 0.18 mmol) was added to a solution of $(NBu_4)(ZH_2)$ (100 mg, 0.18 mmol), NBu_4Br (172 mg, 0.53 mmol) and PPh_4Br (224 mg, 0.53 mmol) in methanol (24 mL). This solution was acidified with glacial acetic acid (2 drops), and a deep red amorphous precipitate formed. This solid was completely converted to red needle crystals over a period of several months. The crystals were collected, washed with methanol and dried in air. Yield: 74 mg (57%). IR (KBr) ν cm^{-1}: 3437, 2960, 1624, 1483, 1375, 1311, 1224, 1179, 937, 894, 663, 603, 466. Elemental anal. (%), found: C, 61.46; H, 4.79; N, 0.80; P, 1.89. Calcd for $(PPh_4)_2(NBu_4)_2[(MoO_2)_4Z_4]\cdot 5H_2O$ ($C_{156}H_{158}Mo_4N_2O_{33}P_2$): C, 61.74; H, 5.25; N, 0.92; P, 2.04.

$(AsPh_4)_3(NBu_4)[(MoO_2)_4Z_4]$ (5). An aqueous solution (1 mL) of $Na_2MoO_4\cdot 2H_2O$ (43 mg, 0.18 mmol) was added to a methanolic solution (25 mL) of $(NBu_4)(ZH_2)$ (100 mg, 0.18 mmol) and $AsPh_4Cl$ (372 mg, 0.89 mmol). This solution was then acidified with glacial acetic acid (2 drops) in methanol (1 mL) to yield a deep red, amorphous precipitate. This solid was completely converted to red, needle crystals upon standing for several months at room temperature. The crystals were collected, washed with methanol and dried in air. Yield: 39 mg (27%). IR (KBr) ν cm^{-1}: 3437, 3056, 2960, 1622, 1482, 1372, 1313, 1225, 1178, 956, 920, 891, 743, 688, 657, 599, 463. UV−vis λ (nm): 526 (max), 554. Elemental anal. (%), found: C, 61.38; H, 4.17; N, 0.40. Calcd for $(AsPh_4)_3(NBu_4)[(MoO_2)_4Z_4]\cdot 2H_2O$ ($C_{164}H_{136}As_3Mo_4NO_{30}$): C, 61.38; H, 4.27; N, 0.44.

$(AsPh_4)_2(NBu_4)_2[(WO_2)_4Z_4]$ (6). An aqueous solution (1 mL) of $Na_2WO_4\cdot 2H_2O$ (59 mg, 0.18 mmol) was added to a solution of $(NBu_4)(ZH_2)$ (100 mg, 0.18 mmol), NBu_4Br (172 mg, 0.53 mmol) and $AsPh_4Cl$ (274 mg, 0.65 mmol) in methanol (25 mL). This red solution was acidified using glacial acetic acid (2 drops), and an immediate orange precipitate was formed. Red crystals with green iridescence formed over several days. The crystals were collected, washed with methanol and dried in air. Yield: 51 mg (34%). IR (KBr) ν cm^{-1}: 3437, 3056, 299, 1624, 1541, 1509, 1485, 1374, 1312, 1225, 1178, 939, 920, 896, 744, 662, 601, 465. Elemental anal. (%), found: C, 54.46; H, 4.44; N, 0.77. Calcd for $(AsPh_4)_2(NBu_4)_2[(WO_2)_4Z_4]\cdot 3H_2O$ ($C_{156}H_{154}As_2Mo_4NO_{31}$): C, 54.50; H, 4.51; N, 0.81.

$(Ph_3PNPPh_3)(NBu_4)_3[(MoO_2)_4Z_4]$ (7). A solution of $Na_2MoO_4\cdot 2H_2O$ (43 mg, 0.18 mmol) in water (1 mL) was added to a methanolic solution (25 mL) of $(NBu_4)(ZH_2)$ (100 mg, 0.18 mmol), Ph_3PNPPh_3Cl (364 mg, 0.63 mmol) and NBu_4Br (172 mg, 0.53 mmol). The deep red solution was acidified using glacial acetic acid (2 drops) to afford a deep red, amorphous solid. This deep red solid was completely converted to red needle crystals over a period of several months. The crystals were collected, washed with methanol and dried in air. Yield: 83 mg (63%). IR (KBr) ν cm^{-1}: 3437, 2962, 1619, 1507, 1483, 1371, 1314, 1226, 1178, 956, 917, 887, 815, 746, 657, 599, 464. UV−vis λ (nm): 526 (max), 554. Elemental anal. (%), found: C, 62.98; H, 5.86; N, 1.90. Calcd for $(Ph_3PNPPh_3)(NBu_4)_3[(MoO_2)_4Z_4]$ ($C_{160}H_{174}Mo_4N_4O_{28}P_2$): C, 63.07; H, 5.76; N, 1.84.

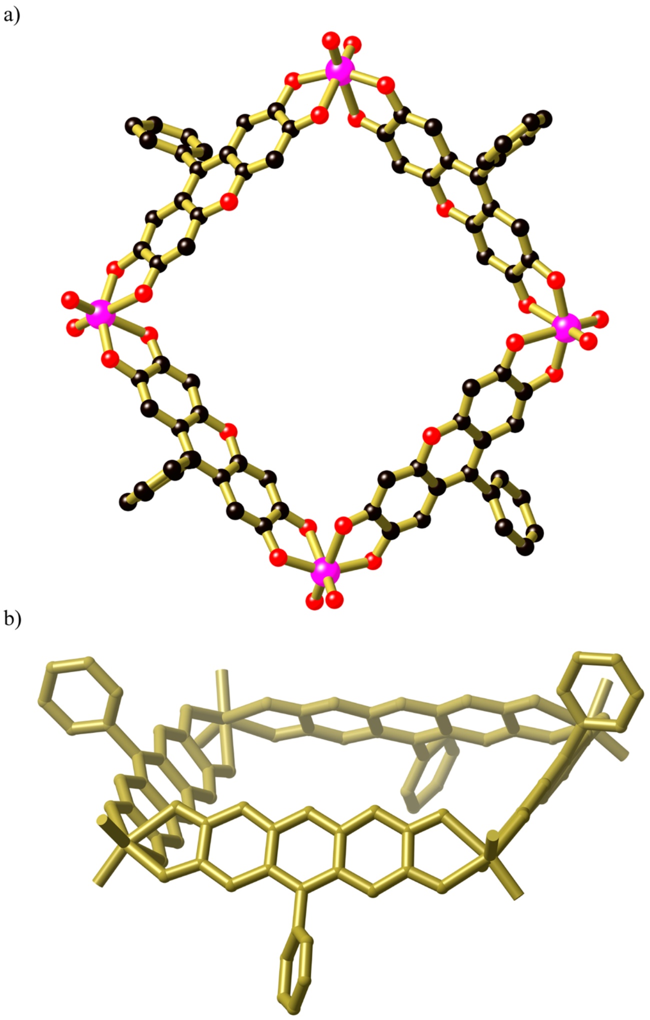

Figure 1. The structure of the $[(WO_2)_4Z_4]^{4-}$ metallocycle in compound **2**, $(MePPh_3)_3(NBu_4)[(WO_2)_4Z_4]$, viewed from (a) on top and (b) almost edge-on. The structures of the metallocycles in all the other compounds reported are similar to the one shown here. Color code: C black, O red, W pink.

$(Ph_3PNPPh_3)(NBu_4)_3[(WO_2)_4Z_4]$ (8). To a methanolic solution (24 mL) of $(NBu_4)(ZH_2)$ (100 mg, 0.18 mmol), Ph_3PNPPh_3Cl (364 mg, 0.63 mmol) and NBu_4Cl (148 mg, 0.50 mmol) was added an aqueous solution (1 mL) of $Na_2WO_4\cdot 2H_2O$ (59 mg, 0.18 mmol). The resulting red solution was acidified with glacial acetic acid (2 drops), and an amorphous orange precipitate was formed. Red prismatic crystals formed amid the orange solid after several days. The crystals were collected, washed with methanol and dried in air. Yield: 42 mg (28%). IR (KBr) ν cm^{-1}: 3439, 2959, 1625, 1513, 1484, 1375, 1312, 1224, 1178, 936, 891, 818, 663, 602, 465. UV−vis λ (nm): 510 (max), 535. Elemental anal. (%), found: C, 54.74; H, 4.87; N, 1.46. Calcd for $(Ph_3PNPPh_3)(NBu_4)_3[(WO_2)_4Z_4]\cdot 5H_2O$ ($C_{160}H_{184}N_4O_{33}P_2W_4$): C, 55.09; H, 5.32; N, 1.61.

$(NEt_4)(NBu_4)_3[(MoO_2)_4Z_4]$ (9). To a methanolic solution (24 mL) of $(NBu_4)(ZH_2)$ (100 mg, 0.18 mmol) and NEt_4Cl (65 mg, 0.39 mmol) was added a solution of $Na_2MoO_4\cdot 2H_2O$ (42 mg, 0.17 mmol) in water (1 mL). The resulting deep red solution was acidified using glacial acetic acid (2 drops) to afford a deep red amorphous precipitate. Upon standing at room temperature for one week deep red needle crystals formed amid this solid. The crystals were collected, washed with

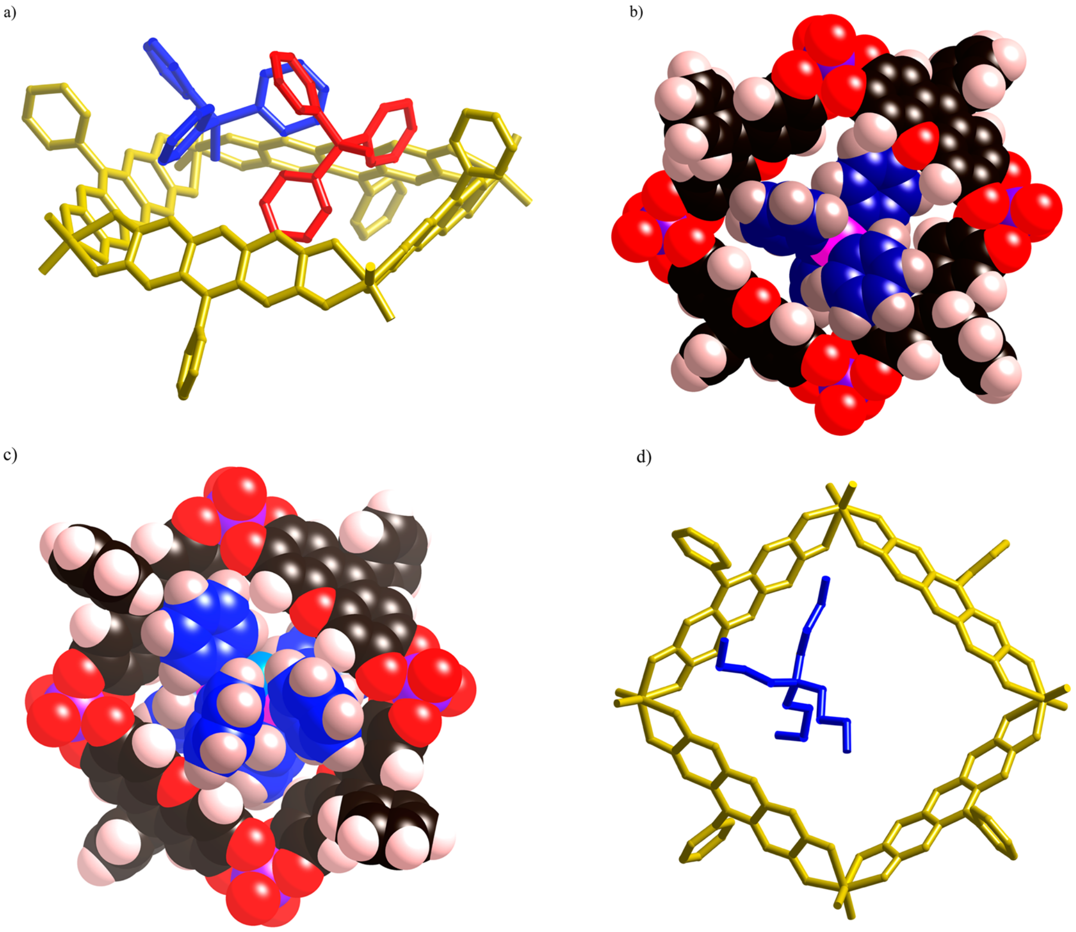

Figure 2. The location of various cations within $[(MO_2)_4Z_4]^{4-}$ metallocycles: (a) A stick representation showing the association of a pair of $PMePh_3^+$ cations (blue and red) with a $[(WO_2)_4Z_4]^{4-}$ metallocycle (gold); (b) a space filling representation showing the inclusion of the $AsPh_4^+$ cation inside a $[(MoO_2)_4Z_4]^{4-}$ metallocycle in compound **5**, $(AsPh_4)_3(NBu_4)[(MoO_2)_4Z_4]$; (c) a space filling representation showing the inclusion of the $Ph_3PNPPh_3^+$ cation inside a $[(MoO_2)_4Z_4]^{4-}$ metallocycle in compound **7**, $(Ph_3PNPPh_3)(NBu_4)_3[(MoO_2)_4Z_4]$; (d) a stick representation showing the association between a NBu_4^+ cation (blue) and a $[(MoO_2)_4Z_4]^{4-}$ metallocycle (gold) in compound **9**, $(NEt_4)(NBu_4)_3[(MoO_2)_4Z_4]$. Color code for space filling representations: C black in metallocycle, blue in cation; H pink; N light blue; O red; P, As pink; Mo purple.

methanol and dried in air. Yield: 45 mg (39%). IR (KBr) ν cm^{-1}: 3460, 2962, 1484, 1313, 1225, 1179, 957, 919, 890, 657, 600, 464. Elemental anal. (%), found: C, 58.71; H, 6.13; N, 2.07. Calcd for $(NEt_4)(NBu_4)_3[(MoO_2)_4Z_4]\cdot 3H_2O$ ($C_{132}H_{170}Mo_4N_4O_{31}$): C, 58.88; H, 6.36; N, 2.08.

Crystallography. Crystals of compounds **1**−**9** in their solvated forms were transferred directly from the mother liquor to a protective oil before being mounted on a goniometer and placed in a stream of nitrogen at 130 K.

X-ray data for compounds **2**·solvate and **4**·solvate were collected on a Bruker CCD SMART diffractometer using Mo Kα radiation while an Oxford Diffraction Xcalibur diffractomer fitted with Cu Kα radiation was used to collect data on the remaining compounds. All structures were solved using direct methods and refined using a least-squares refinement based on F^2 (SHELX-97).[8] Crystallographic analysis was performed using the WinGX system of programs.[9] Details relating to crystal data and structure refinement are presented in Table 1. While the $[(MO_2)_4Z_4]^{4-}$ (M = Mo, W) metallocycles were well-defined in the crystallographic analyses, considerable disorder was apparent with some of the cations and solvent molecules. For structures **1**·solvate and **9**·solvate the SQUEEZE routine in PLATON was used to treat highly disordered solvent in the crystal structures.[10] A discussion of the treatment of the disorder in the structures is presented in the Supporting Information.

ESI Mass Spectrometry. An Agilent 6520A Q-TOF with attached Agilent 1200 Series binary pump and autosampler was used with the instrument set to the following conditions: negative ion mode, drying gas heater = 300 °C, drying gas = 7 L·min^{-1}, nebulizer = 32 psi, fragmentor = 125 V, skimmer = 65 V, capillary voltage = 3000 V, scan range 50−3000 m/z. Acetonitrile was used as the mobile phase with a 1−5 μL injection and a flow rate of 250 μL·min^{-1} monitored for 1.5 min.

■ RESULTS AND DISCUSSION

ZH_3 itself, because of its insolubility, is not a very convenient starting material for the preparation of metal derivatives of Z^{3-}. The more soluble $(NBu_4)(ZH_2)$ can be easily obtained by reaction of ZH_3, NBu_4Br and $NEt^{i}Pr_2$ (Hünig's base) in boiling DMF and affords a more convenient source of Z^{3-} for the metal complexes.

Addition of acetic acid to mixtures of $Na_2(MO_4)$ (M = Mo or W) in water together with $(NBu_4)(ZH_2)$ in MeOH containing in addition various quaternary ammonium, phosphonium or arsonium salts gives a range of crystalline solids containing $[(MO_2)_4Z_4]^{4-}$ (M = Mo, W) metallocycles. When $(NBu_4)(ZH_2)$ is used as the source of Z^{3-}, the products incorporate NBu_4^+ cations to varying degrees and commonly have compositions $(NBu_4)_n(X)_{4-n}[(MO_2)_4Z_4]$ where X^+ is some other quaternary ammonium, phosphonium or arsonium cation. The following combinations of $[(MO_2)_4Z_4]^{4-}$ and countercations (variously solvated) were isolated and structurally characterized: compound **1**, $(MePPh_3)_3(NBu_4)[(MoO_2)_4Z_4]$; compound **2**,

$(MePPh_3)_3(NBu_4)[(WO_2)_4Z_4]$; compound **3**, $(MePPh_3)_4[(WO_2)_4Z_4]$; compound **4**, $(PPh_4)_2(NBu_4)_2[(MoO_2)_4Z_4]$; compound **5**, $(AsPh_4)_3(NBu_4)[(MoO_2)_4Z_4]$; compound **6**, $(AsPh_4)_2(NBu_4)_2[(WO_2)_4Z_4]$; compound **7**, $(Ph_3PNPPh_3)(NBu_4)_3[(MoO_2)_4Z_4]$; compound **8**, $(Ph_3PNPPh_3)(NBu_4)_3[(WO_2)_4Z_4]$; compound **9**, $(NEt_4)(NBu_4)_3[(MoO_2)_4Z_4]$. The metallocycles in all of these compounds have very similar structures, with the four metal centers located at the corners of a slightly distorted square. The distortion, which occurs to varying degrees, is toward a rhombus and also toward a tetrahedron. The general metallocycle structure is presented in Figure 1, which shows the macrocycle of compound **2**. With each metal center coordinated by *cis* oxo groups and a pair of chelating ligands, the individual metal centers are chiral with absolute configurations alternating in the order Λ, Δ, Λ, Δ around the metallocycle. In its most symmetrical conformation, the cationic metallocycle is achiral with point group symmetry of D_{2d}; however, in each of the nine crystal structures the asymmetric unit contains a complete metallocycle, which adopts a chiral conformation. Compounds **1**−**8** crystallize in the space group $P\bar{1}$ with the crystals containing a racemic mixture of the enantiomeric conformations of the metallocycles. Compound **9** crystallizes in the chiral space group $C2$, and thus individual crystals contain only one enantiomeric conformation of the metallocycle.

Metal···metal separations along the edges of the metallocycles range between 12.75 and 12.91 Å for the Mo derivatives and 12.78 and 12.90 Å for the W systems. The degrees of tetrahedral and rhombic distortion of the metallocycles away from a square M_4 arrangement vary from one system to another, although in no case are they very large, e.g., M···M···M angles lie in the range 95.2° to 84.7° and M···M "diagonals" vary from 17.41 Å to 18.01 Å for the short diagonal in each metallocycle and from 18.31 to 18.82 Å for the long diagonal. Presumably the distortion adopted in any case is such as to maximize the attractive forces between the $[(MO_2)_4Z_4]^{4-}$ anion and the contacting species (cations, solvent molecules and to a lesser extent neighboring anionic metallocycles) both "inside" and "outside" the ring. The Z^{3-} ligands are "bowed out" to varying but small extents; in some cases there is negligible bowing, the two metal centers attached to the ligand lying very close to the plane of the ligand, whereas in other cases the central atoms of the ligand are located somewhat to the "outside" of the line between the two metal centers (that is to say "outside" relative to the interior of the metallocycle). As can be seen in Figure 1 the planes of the (essentially planar) Z^{3-} ligands are significantly inclined to the average M_4 plane such that two phenyl groups on opposite sides of the metallocycle point upward and outward and the other two point downward and outward. The oxygen atoms of the central heterocyclic ring are thus closer to the center of the metallocycle than are the C9 carbon atoms; the distances between the van der Waals surfaces of the oxygen atoms on opposite sides of the metallocycle vary between approximately 8.0 and 10.7 Å, which gives some indication of the size of the central cavity.

Some of the cations, together in some cases with disordered solvent molecules, are located within the tetra-anionic metallocycle. In those compounds containing aromatic-based cations as well as NBu_4^+ (i.e., **1**, **2** and **4**−**8**), the aromatic cation is bound inside the metallocycle in preference to the NBu_4^+, secured by either edge-to-face or face-to-face interactions with the Z^{3-} units. In **3** the $PMePh_3^+$ cations are the sole cations, and these are located both inside and outside the metallocycle cavity. Two $(PMePh_3)^+$ cations associate with the interior of the metallocycle, as shown in Figure 2a, but neither approaches the central region of the metallocycle. In contrast the $[(MoO_2)_4Z_4]^{4-}$ metallocycle encircles a $[AsPh_4]^+$ cation in compound **4** as shown in Figure 2b;. The larger cation, $(Ph_3PNPPh_3)^+$, in compound **7**, $(Ph_3PNPPh_3)(NBu_4)_3[(MoO_2)_4Z_4]$, is better able to fill the central space available and make multiple contacts with the metallocycle (Figure 2c). Turning to systems devoid of aromatic-based cations, the NBu_4^+ cation in compound **9**, $(NEt_4)(NBu_4)_3[(MoO_2)_4Z_4]$, is bound inside the metallocycle in preference to the smaller NEt_4^+ cation, as indicated in Figure 2d. The inclusion of solvent molecules in the metallocycle cavity presumably results from the imperfect match of the size and shape of the cations with the internal cavity of the metallocycle leading to the generation of spaces of an appropriate size for solvent molecules.

All compounds, except **9**, crystallize in the space group $P\bar{1}$, and in each of these structures the mean planes of the metallocycles are approximately parallel. Compounds **1**−**3**, which are the only ones to include $PMePh_3^+$ cations, have very similar unit cell dimensions, and very similar dispositions of the metallocycles. The three compounds all display a pair self-complementary C−H···O hydrogen bonds (~3.28 Å) that extend between a pair of metallocycles related by a center of inversion as indicated in Figure 3. The metallocycles in this trio of compounds in the extended structure are all arranged as indicated in Figure 4a, which shows the arrangement of pairs of closely associated metallocycles. Within compounds **4**−**8** the distribution of metallocycles is similar but different from that in compounds **1**−**3**. The metallocycles are reasonably well separated although hydrogen atoms of phenyl groups of one metallocycle do interact with oxygen atoms in neighboring metallocycles. Similar interactions involving phenyl groups are also apparent in compounds **1**−**3**. The arrangement of the metallocycles in compounds **4**−**8** is indicated in Figure 4b.

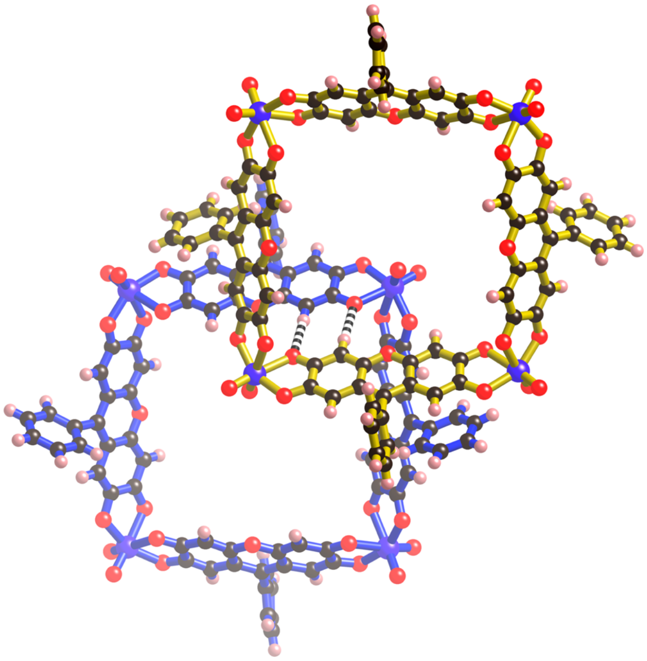

Figure 3. A pair of centrosymmetrically related metallocycles linked by a pair of self-complementary hydrogen bonds in $(PMePh_3)_4[(WO_2)_4Z_4]$ (**3**). C−H···O hydrogen bonds are indicated by striped connections. Similar interactions are present in compounds **1** and **2**.

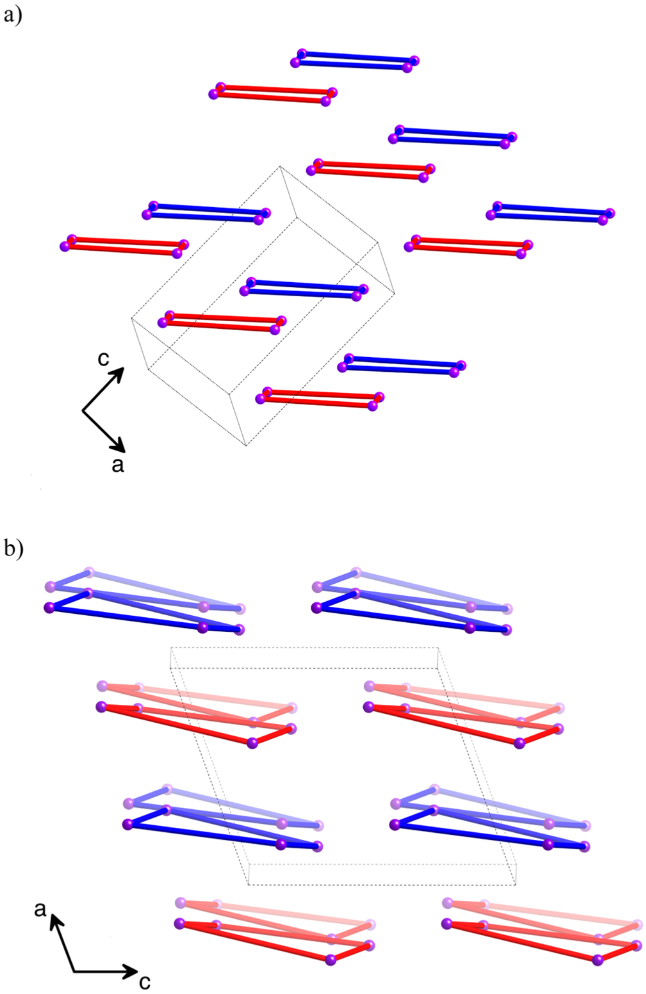

Figure 4. Schematic representations of the arrangement of metallocycles within (a) compound **2**; a similar arrangement is present in compounds **1** and **3**; and (b) compound **5**; a similar arrangement is present in compounds **4** and **6**−**8**. For simplicity only the metal centers of the metallocycles are represented. Metallocyclic conformers with the same absolute configuration in the crystal structure are the same color in each figure.

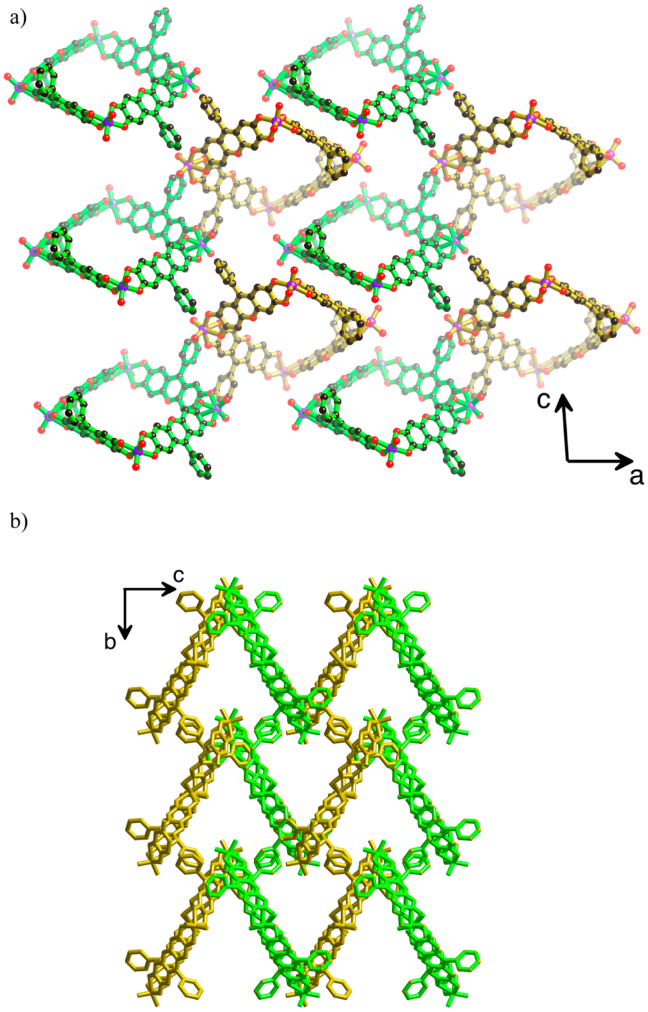

Figure 5. The arrangement of the metallocycles in compound **9**, $(NEt_4)(NBu_4)_3[(MoO_2)_4Z_4]$, showing (a) the metallocycles in a single corrugated sheet and (b) an edge-on view to the stacked corrugated sheets. All metallocycles adopt conformations that have the same absolute conformation; the mean planes of all green metallocycles are parallel, and the planes of all gold metallocycles are parallel.

$(NEt_4)(NBu_4)_3[(MoO_2)_4Z_4]$, **9**, crystallizes in the chiral space group C2, and all the metallocycles adopt the same enantiomeric conformation. While individual crystals are chiral, the bulk sample is presumed to represent a racemic mixture of crystals. The compound is unique among the compounds reported here in that the average planes of half the metallocycles are inclined to those of the other half. Metallocycles of both orientations are arranged in corrugated parallel sheets as shown in Figure 5a. Within the corrugated sheets there are pairs of closely associated metallocycles (Figure 5b), related to each other by a 2-fold axis. The metallocycles within each of the pairs make a number of face-on atom-to-atom contacts involving one ligand from each metallocycle; in particular there is a remarkably short heterocyclic oxygen-to-heterocyclic oxygen separation of 2.93 Å. The corrugated sheets stack as indicated in Figure 5b.

The gas phase anionic species generated by the metallocyclic compounds in the electrospray ionization mass spectrometer were examined using acetonitrile solutions. A list of the most abundant ions observed for each compound is presented in Table 2. The metallocycle remains intact in the gas phase, the major peaks in all cases corresponding to either $[(MO_2)_4Z]^{4-}$ or its protonated form, $\{H\text{-}[(MO_2)_4Z_4]\}^{3-}$. For the most abundant ions, each isotopic peak is separated by either 0.25 or 0.3333 m/z units, indicating a multiple charge state of −4 or −3 respectively. Retention of the metallocyclic structure is confirmed by accurate mass and comparison of the observed isotopic peak profile with calculated isotopic peak profiles. Results indicate accurate mass matches to less than 5 ppm for calculated molecular formulas and a complete match of observed and calculated isotopic peak profiles in all cases indicating the presence of the metallocyclic structure. Trianions of the type $\{X\text{-}[(MO_2)_4Z_4]\}^{3-}$, in which $[(MO_2)_4Z_4]^{4-}$ is associated with one of the counter cations, X^+, are observed in all cases. Often where NBu_4^+ and some other cation, X^+, are present in the same compound, both $\{(NBu_4)\text{-}[(MO_2)_4Z_4]\}^{3-}$ and $\{X\text{-}(MO_2)_4Z_4]\}^{3-}$ are observed. It does appear that the $[(MO_2)_4Z_4]^{4-}$ metallocycle is not very discriminating in its choice of which cation to associate with, the relative intensities of the two peaks corresponding to $\{(NBu_4)\text{-}[(MO_2)_4Z_4]\}^{3-}$ and $\{X\text{-}[(MO_2)_4Z_4]\}^{3-}$, varying from compound to compound. It would appear that none of the cations used here are particularly complementary to the relatively rigid and regular $[(MO_2)_4Z_4]^{4-}$ interior; thus, for example, the

Table 2. Major Ions Detected by ESI-MS in the Negative Ion Mode

		m/z			
compound	anion	exptl	calcd	error (ppm)	rel abund
$(PMePh_3)_3(NBu_4)$ $[(MoO_2)_4Z_4]$ **1**	$[(MoO_2)_4Z_4]^{4-}$	446.9441	446.9402	8.7	100
	$\{PMePh_3[(MoO_2)_4Z_4]\}^{3-}$	688.2974	688.2919	8.0	60
	$\{NBu_4[(MoO_2)_4Z_4]\}^{3-}$	676.6870	676.6819	7.5	35
$(PMePh_3)_3(NBu_4)$ $[(WO_2)_4Z_4]$ **2**	$[(WO_2)_4Z_4]^{4-}$	532.9887	532.9854	6.2	100
	$\{PMePh_3[(WO_2)_4Z_4]\}^{3-}$	803.0220	803.0192	3.5	47
	$\{NBu_4[(WO_2)_4Z_4]\}^{3-}$	791.4127	791.4093	4.3	23
$(PMePh_3)_4$ $[(WO_2)_4Z_4]$ **3**	$[(WO_2)_4Z_4]^{4-}$	532.9881	532.9854	5.1	100
	$\{PMePh_3[(WO_2)_4Z_4]\}^{3-}$	803.0214	803.0192	2.7	42
$(PPh_4)_2(NBu_4)_2$ $[(MoO_2)_4Z_4]$ **4**	$[(MoO_2)_4Z_4]^{4-}$	446.9423	446.9399	5.4	100
	$\{PPh_4[(MoO_2)_4Z_4]\}^{3-}$	708.9967	708.9637	4.2	60
	$\{NBu_4[(MoO_2)_4Z_4]\}^{3-}$	676.6835	676.6819	2.3	35
$(AsPh_4)_3(NBu_4)_2$ $[(MoO_2)_4Z_4]$ **5**	$[(MoO_2)_4Z_4]^{4-}$	446.9428	446.9399	6.5	100
	$\{AsPh_4[(MoO_2)_4Z_4]\}^{3-}$	723.6160	723.6130	4.1	61
	$\{NBu_4[(MoO_2)_4Z_4]\}^{3-}$	676.6854	676.6819	5.2	36
$(AsPh_4)_2(NBu_4)_2$ $[(WO_2)_4Z_4]$ **6**	$[(WO_2)_4Z_4]^{4-}$	532.9826	532.9854	−5.3	100
	$\{NBu_4[(WO_2)_4Z_4]\}^{3-}$	791.4058	791.4093	−4.4	42
	$\{AsPh_4[(WO_2)_4Z_4]\}^{3-}$	838.3363	838.3404	−4.9	38
	$\{H[(WO_2)_4Z_4]\}^{3-}$	710.9802	710.9836	−4.8	31
$(Ph_3PNPPh_3)(NBu_4)_3]$ $[(MoO_2)_4Z_4]$ 7	$[(MoO_2)_4Z_4]^{4-}$	446.9428	446.9399	6.5	100
	$\{NBu_4[(MoO_2)_4Z_4]\}^{3-}$	676.6854	676.6819	5.2	55
	$\{Ph_3PNPPh_3[(MoO_2)_4Z_4]\}^{3-}$	775.3199	775.3154	5.8	23
$(Ph_3PNPPh_3)(NBu_4)_3$ $[(WO_2)_4Z_4]$ **8**	$[(WO_2)_4Z_4]^{4-}$	532.9880	532.9854	4.9	100
	$\{NBu_4[(WO_2)_4Z_4]\}^{3-}$	791.4127	791.4093	4.3	56
	$\{Ph_3PNPPh_3[(WO_2)_4Z_4]\}^{3-}$	890.0474	890.0428	5.2	25
$(NEt_4)(NBu_4)_3$ $[(MoO_2)_4Z_4]$ **9**	$\{H[(WO_2)_4Z_4]\}^{3-}$	596.2589	596.2568	3.5	100
	$[(WO_2)_4Z_4]^{4-}$	446.9431	446.9408	5.1	76
	$\{H_2[(MoO_2)_4Z_4]\}^{2-}$	894.8928	894.8888	4.5	30
	$\{NBu_4[(MoO_2)_4Z_4]\}^{3-}$	676.6861	676.6825	5.3	12
	$\{NEt_4[(MoO_2)_4Z_4]\}^{3-}$	639.3097	639.3074	3.6	2

$(Ph_3PNPPh_3)^+$ cation in compound **7**, $(Ph_3PNPPh_3)(NBu_4)_3[(MoO_2)_4Z_4]$, occupies the cavity of the metallocycle in the crystalline phase, but in the gas phase the $\{NBu_4\text{-}[(MO_2)_4Z_4]\}^{3-}$ anion is more abundant than the $\{Ph_3PNPPh_3\text{-}[(MO_2)_4Z_4]\}^{3-}$ species, which may reflect the availability of three NBu_4^+ cations for every $(Ph_3PNPPh_3)^+$. In compound **9** the $\{NBu_4\text{-}[(MO_2)_4Z_4]\}^{3-}$ ion predominates over the $\{NEt_4\text{-}[(MO_2)_4Z_4]^{3-}\}$ species, presumably because the smaller NEt_4^+cation rattles around less comfortably inside the metallocycle, but nevertheless the trianions in which these smaller cations are bound are observed. In a few cases, peaks corresponding to the association of two cations with Z^{4-} are observed, e.g., $\{(PMePh_3)_2\text{-}[(MO_2)_4Z_4]\}^{2-}$.

Metallocycles have been previously reported in which $M^{VI}O_2^{2+}$ centers are combined with certain bis-catecholate ligands superficially related to Z^{3-}. Duhme and co-workers isolated MoO_2^{2+} [2 + 2][7a−c] and [3 + 3][7d] metallocycles using a variety of bis-catecholate ligands. The 4,4-(9*H*-fluorene-9,9-diyl)di(benzene-1,2-diol) also affords [2 + 2] $M^{VI}O_2^{2+}$ metallocycles.[7e] In these previously reported metallocycles each ligand shows a significant bend, which is in contrast to the fluorone systems reported here.

In summary, we report here a series of MoO_2- and WO_2-derived [4 + 4] metallocycles containing the trianionic bridging ligand 9-phenyl-2,3,7-tris(olate)-fluor-6-one. In each of the crystal structures the individual metallocycles adopt a chiral conformation; however, in all cases except for compound **9**, both enantiomeric forms are present in each crystal. Being anionic, these metallocycles bind a number of cations in their cavities. ESI mass spectrometry shows that the metallocycles remain intact in the gas phase and associate with organic cations, X^+, to form $[X\text{-}[(MO_2)_4Z_4]]^{3-}$ and in some cases $\{X_2\text{-}[(MO_2)_4Z_4]\}^{2-}$ species. The $[(MO_2)_4Z_4]^{4-}$ metallocycles appear not very discriminating in their choice of the cations with which they associate.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

Discussion relating to the treatment of disorder in the crystal structures. Crystallographic data in CIF format. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

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