

An Effective Core Potential Study of Transition-Metal Chalcogenides. 1. Molecular Structure

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Abstract: A structural analysis is reported of roughly 150 transition-metal (TM)–chalcogenido complexes in a variety of chemical environments. With few exceptions, agreement between calculated and experimental geometries is excellent. The research provides convincing evidence that computational methods employed are adequately describing the bonding in these diverse TM complexes. Interesting trends in relative TMCh ($R_{MCh}-R_{MCh}$) bond lengths are found. Experimental and computational data show that other than the zirconocene- and hafnocene-oxos there is similar behavior in relative bond lengths for widely varying TM–chalcogenido complexes. Relative bond lengths versus oxo (S–O, Se–O, and Te–O) in group IVB metallocenes tend to be larger than for other families of complexes and show less variation among the heavier chalcogens (Se–S, Te–S, and Te–Se). Analysis of localized wave functions for Cp_2ZrCh point to a greater contribution from a singly-bonded Zr–Ch structure (relative to Zr=Ch) when Ch is O compared to heavier chalcogens. Taken together, the data suggest that there is a fundamental difference in the Zr–oxo (and Hf–oxo) bond in relation to heavier chalcogens, consistent with recent experimental data. In previous studies of multiply bonded TM complexes we have focused on the ability of ECPs to make computations feasible for complexes incorporating even the heaviest transition metals. The present work also evaluates ECP methods for heavier main group (MG) elements. The chalcogens (Ch) O, S, Se, and Te are included in this study.

Introduction

Among complexes with a multiple bond between a transition-metal (TM) and main group (MG) element, chalcogens (Ch) are probably the most studied in terms of molecular and vibrational structure, particularly for the lightest member of the series—oxo ($L_nM=O$) complexes. An overview of oxo structure and bonding can be found in reviews by Mayer and Nugent,² Griffith,³ and Holm.⁴ Müller has reviewed d^0 sulfidos and selenidos.⁵ Roof and Kolis have recently reviewed the literature for selenido and tellurido complexes including some terminally-bound examples.⁶ Oxo complexes have received the most attention, because of their intermediacy in biochemical (e.g., cytochrome P-450⁷) and industrial (e.g., conversion of propylene to acrolein⁸) oxidations. Apart from fundamental interest in TM=MG multiple bonding for heavier main group elements, TM–chalcogen complexes have received attention in connection with the design of molecular precursors to solid-state materials.⁹ Terminal sulfidos are of interest in connection with biochemical systems such as xanthine oxidase.¹⁰ Recent synthetic efforts have produced the first terminally-bound tellurido complex by Rabinovich and Parkin,¹¹ *trans*- $W(PMe_3)_4(Te)_2$, which was quickly followed by examples

from Christou and Arnold: Zr and Hf (Te)(sitol)₂(dmpe)₂, sitol = $TeSi(SiMe_3)_3$; dmpe = 1,2-bis(dimethylphosphino)ethane.¹² Howard and Parkin have reported an entire series of chalcogenido complexes $Cp'_2M(Ch)(py)$ for M = Zr and Hf, Ch = O, S, Se, Te; $Cp' = \eta^5-C_5Me_4Et$; py = pyridine.¹³ Page et al. have published electron diffraction studies of $W(X)_4(Ch)$, X = F, Br, Cl and Ch = O, S, Se.¹⁴ Finally, there are the well-known metallates, $[MO_4]^{4-}$, as well as sulfido and selenido congeners.^{2–5}

The present contribution is a continuation of computational studies of TM=MG bonding,¹⁵ the focus of which is developing computational approaches to complexes incorporating metals from the entire d-block. Two main questions are addressed in this paper. First, are computational methods capable of predicting the structure of TM chalcogenido complexes? In previous studies we have employed effective core potential (*vide infra*) methods to study multiple bonding; with few exceptions we have found the computational scheme to perform quite well with respect to structural prediction.¹⁵ Second, what approaches are appropriate to the chemistry of the heavier MG elements? In previous work we have sought to highlight opportunities methodological advances provide in the study of the heaviest TMs.¹⁵ Chalcogenido complexes provide an excellent opportunity to explore the heavier

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MG elements. In addition to the large database of structural information, chalcogenido complexes are one of the few families of TM complexes for which there is extensive vibrational data for complexes in varied chemical environments,²⁻⁶ bringing us to a third point of interest, to be addressed in a companion paper. Can a simple computational scheme predict the vibrational structure of TM complexes? Ab initio methods have been successfully applied to estimation of vibrational spectra for main group bonds.¹⁶ However, to our knowledge, no systematic investigation for a family of related TM complexes has been reported. In the present contribution the focus is on the bonding and structure of chalcogenidos with relatively simple ligand sets (e.g., halides) that have been the subject of structural and/or vibrational analysis.

Computational Methods

Calculations employ the program GAMESS running in serial, parallel, and vector mode.¹⁷ An iPSC/860 (Oak Ridge National Lab), Paragon (San Diego Supercomputing Center, SDSC), CM-5 (University of Tennessee-Knoxville), and SP-1 (Cornell National Supercomputer Facility) were used as parallel platforms. Calculations also employed vectorized GAMESS on the Cray Y-MP/868 at SDSC and the serial version of GAMESS at Memphis State (RS-6000/350).

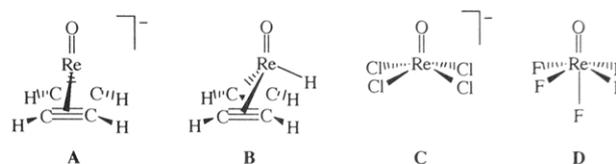
Our main approach to the challenges of computational d- and f-block chemistry is the design and testing of effective core potentials (ECPs).¹⁸ Great savings in time, memory, and disk space are effected by replacing chemically less important core electrons and orbitals with a small number of ECPs. Effective core potentials (ECPs) and valence basis sets are used for heavy atoms and the -31G basis set for H. ECPs replace the innermost core orbitals for the TMs and all core orbitals for main-group (MG) elements.¹⁸ Thus, the ns, np, nd, ($n+1$)s, and ($n+1$)p are treated explicitly for the d-block;^{18a} for the main-group, ns and np are treated explicitly.^{18b} In the standard implementation, TM valence basis sets are quadruple- and triple- ζ for the sp and d shells, respectively, while main-group elements have a double- ζ valence basis.^{18a,b} Basis sets for MG elements are augmented with a d polarization function.¹⁹ Bond lengths and angles for TM=MG complexes are typically predicted to within 1–3% of experiment using the present scheme.¹⁵ From a chemical standpoint, ECPs afford great leeway in the choice of interesting problems since calculations on congeners within a group are carried out with near equal facility.

Geometries are optimized at the restricted Hartree-Fock (RHF) level for closed-shell singlets, unless otherwise specified; for open-shell systems a restricted open-shell Hartree-Fock wave function (ROHF) is used. Vibrational frequencies are calculated at stationary points to identify them as minima or transition states. Intrinsic stretching frequencies, and force constants derived from them, were calculated using the method of Boatz and Gordon.²⁰

Results

1. Geometries. a. $L_nM(\text{Ch})$ Complexes. Mono oxo complexes come in a wide variety of oxidation states, ligand sets, and coordination geometries with structurally characterized examples ranging from the Ti²⁺¹³ to Co-triad.²¹ This richness of chemical environments is an ideal test for flexibility of the ECP scheme. A preliminary study using the present ECP approach has been

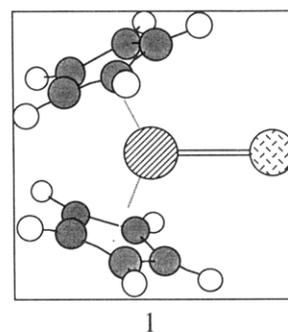
reported for Re-oxos;²² formal oxidation states of the Re-oxo complexes are +1, +3, +5, and +7, and coordination numbers (counting acetylene as a monodentate ligand) range from 3 to 6, A–D. Parallel-GAMESS and



ECP methods quickly predicted bond lengths and bond angles of these chemically distinct Re-oxo complexes to within a few hundredths of an Å and 3° (i.e., errors of only 1–3%), respectively.²² A more systematic study of the major structural motifs for chalcogenido complexes is given below.

i. MX_2Ch Complexes. The low coordination number of an MX_2Ch complex is expected to limit structurally characterized examples to systems where X is bulky enough to engender kinetic stability. Examples of the MX_2Ch structural motif are $\text{Cp}'_2\text{MCh}$ where M is a group IVB (Ti, Zr, Hf) metal.^{13,23–28} Structurally characterized complexes have a fourth (py or substituted-py) ligand, although there is evidence that transient $\text{Cp}'_2\text{MCh}$ is formed in solution.^{25–27} The complexes Zr and Hf-(Te)(site)₂ can be considered as being of the MX_2Ch type with two bidentate dmpe ligands coordinated for a total coordination number of 7.¹² At an opposite extreme from high-valent, Ti-triad chalcogenides are bis(alkyne)Re-oxo anions which were first isolated as $[\text{Na}(\text{MeCN})_2]^+$ -bridged dimers²⁹ and recently in monomeric form by sequestering the Na^+ counter ion in a cryptand.²² A more indepth ECP analysis of $[\text{Re}(\text{O})(\text{HCCH})_2]^-$ has been published elsewhere.²²

Until recently, there have been few structurally characterized, terminal chalcogenidos of group IVB metals.¹³ The main examples were limited to titanyl complexes of porphyrin and porphyrin-like ligands.^{30–36} Andersen et al. have structurally characterized $\text{Cp}^*_2\text{Ti}(\text{O})(4\text{-phenyl-py})$.²³ The availability of parallel computing resources makes feasible a study of metallocene models ($\text{Cp}_2\text{M}(\text{Ch})$), M = Ti, Ch = O; M = Zr, Hf; Ch = O, S, Se, Te. Metallocene models, **1**,



were optimized under C_{2v} symmetry; results are collected in Table

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Table 1. Cp₂M(Ch) Complexes

	Ti/O ^a	Zr/O	Zr/S	Zr/Se	Zr/Te	Hf/O	Hf/S	Hf/Se	Hf/Te
M-Ch	1.61 Å	1.76 Å	2.28 Å	2.42 Å	2.68 Å	1.76 Å	2.28 Å	2.41 Å	2.67 Å
M-Cp ^b	2.15 Å	2.34 Å	2.29 Å	2.29 Å	2.27 Å	2.31 Å	2.27 Å	2.26 Å	2.25 Å
Cp-M-Cp	132°	131°	131°	131°	132°	131°	131°	131°	133°
ν_{MCh}^c	1059	945	484	328	248	933	462	293	213
k_{MCh}^c	7.92	7.15	3.25	2.68	1.92	7.53	3.42	2.80	2.01

^a Geometries of these models, **1**, were calculated as described in the Computational Methods section. ^b The centroid of the $\eta^5\text{-C}_5\text{H}_5$ ring is denoted Cp. ^c Intrinsic stretching frequencies (ν_{MCh} , in cm^{-1}) and MCh force constants (k_{MCh} , in mdyn \AA^{-1}) are calculated using the method of Boatz and Gordon.²⁰

1. The Ti-oxo bond length in Cp₂TiO is 1.61 Å, in good agreement with Cp*₂Ti(O)(4-phenyl-py) which has a TiO bond length of 1.665(3) Å.²³ Titanium-oxo bond lengths from 1.613(5) Å to 1.653(3) Å have been reported for other titanyl complexes.³⁰⁻³⁴ The Ti-Cp (Cp is the centroid of the $\eta^5\text{-C}_5\text{H}_5$ ring) distance in Cp₂TiO is 2.15 Å, compared to 2.20 Å in Cp*₂Ti(O)(4-phenyl-py).

A preliminary account of ECP studies of CpM(Ch) complexes can be found in refs 13a and 13b along with metric data for experimental models. As noted,¹³ there is excellent agreement between calculated and experimental¹³ ((Cp')₂M(py)(Ch) in parentheses) ZrCh and HfCh bond lengths: ZrO = 1.76 Å (1.804(4) Å), ZrS = 2.28 Å (2.334(2) Å), ZrSe = 2.42 Å (2.480(1) Å), and ZrTe = 2.68 Å (2.729(1) Å); HfO = 1.76 Å (1.826(9) Å); HfS = 2.28 (2.311(3) Å); HfSe = 2.41 Å (2.467(1) Å); HfTe = 2.67 Å (2.716(1) Å), an average difference of only 2% for the entire series. Trends in bond lengths also show excellent agreement, e.g., ZrS-ZrO = 0.52 Å (0.53 Å, experimental), ZrSe-ZrO = 0.66 Å (0.68 Å, experimental), ZrTe-ZrO = 0.92 Å (0.93 Å, experimental). Calculated Zr-Cp distances are \approx 2.3 Å for **1**, as found experimentally;¹³ similar good agreement is found for hafnocenes. The excellent results for a series of calculations ranging from a TiO analogue to its HfTe congener, obtained with equal computational facility, is a powerful exhibition of the utility of ECP methods in accessing chemistry of the entire Periodic Table.

ii. M(X)₃Ch Complexes. Four-coordinate oxos are not prevalent; in the compendium of Nugent and Mayer² the only structurally characterized examples are VCl₃O and Ta(O)[N(i-Pr)₂]₃. The complex VCl₃O has been studied by gas-phase electron diffraction:³⁷ VO = 1.56(4) Å (1.50 Å, calcd); VCl = 2.12(3) Å (2.14, calcd); OVCl = 108(2)° (109°, calcd). Complexes of NbOCl₃ with two neutral bases have been characterized:³⁸ NbO bonds in mer-Nb(O)(Cl)₃(hmpa)₂ and mer-Nb(O)(Cl)₃(MeCN)₂ are 1.692(5) Å and 1.68(2) Å, consistent with the calculated value of NbO = 1.65 Å in the C_{3v} minimum of NbCl₃O. The calculated TaO bond length in TaCl₃O, 1.67 Å, is shorter by 3% than the TaO bond length in TaO(N(i-Pr)₂)₃, 1.725(7) Å.²

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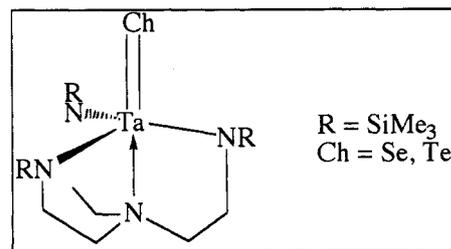
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MX₃S complexes, X = halide, have been structurally characterized with additional ligands coordinated to the TM, Table 2. The complexes MCl₃S (M = V, Nb, Ta) possess C_{3v} minima and calculated TM-sulfido bond lengths of 1.94 Å (V), 2.11 Å (Nb) and 2.12 Å (Ta). The V^{IV} complex VS(acen), acen = N,N'-ethylenebis(acetylacetonate iminate), has VS = 2.061(1) Å,³⁹ considerably longer than in VCl₃S probably due in part to the change in oxidation state. The SPPPh₃ adduct of NbCl₃S has Nb-sulfido = 2.114(4) Å, very close to the calculated value; the SPPPh₃ ligand in this adduct is trans to the sulfido making it unclear to what extent this lengthens the Nb-sulfido bond over that in a base-free complex.⁴⁰ The calculated TaS bond length of 2.12 Å in TaCl₃S is shorter than the average of the eight reported terminal Ta^{VS} bond lengths, 2.18 Å, (Ta(S)(Cl)₃-(PhSCH₂CH₂SPh),⁴¹ STa(S₂CNEt₂)₃,⁴² six terminal TaS bonds in Ta₆S₁₇⁴⁺),⁴³ which is not surprising given the larger coordination numbers of experimental models.

Simple Cl₃TaCh models of recently reported selenido and tellurido complex, **2**,⁴⁴ were



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studied. The TaSe and TaTe bond lengths in TaCl₃Ch are 2.24 and 2.47 Å, respectively, a difference of 0.23 Å; experimental bond lengths in **2-Se** and **2-Te** are 2.330(1) Å and 2.568(1) Å,^{44a} a difference of 0.24 Å. Using the Ta-oxo bond length in TaCl₃O as a standard, Table 2, shows that ECPs yield excellent reproduction of trends as well as providing quantitative prediction of metric data: TaS-TaO = 0.45 Å (0.45 Å, experimental), TaSe-TaO = 0.57 Å (0.60 Å, experimental), TaTe-TaO = 0.80 Å (0.84 Å, experimental).^{2,41-44} As with the group IVB metallocene complexes, there is good agreement for TM-chalcogenido bond lengths between computational and experimental models both in absolute and relative terms. Finally, note that TMCh bond length differences relative to the oxo analogue are much higher (by \approx 0.1 Å) in the Ta case than in the group IVB systems, a point

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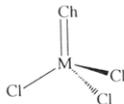
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Table 2. MCl₃Ch Complexes^a

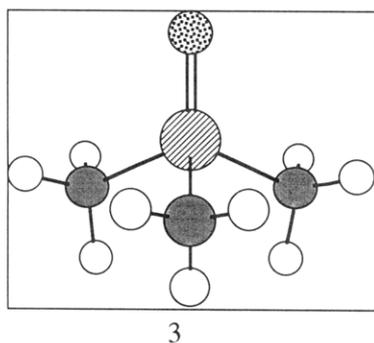
	V/O	Nb/O	Ta/O	V/S	Nb/S	Ta/S	Ta/Se	Ta/Te
M–Ch	1.50 Å	1.65 Å	1.67 Å	1.94 Å	2.11 Å	2.12 Å	2.24 Å	2.47 Å
M–Cl	2.14 Å	2.31 Å	2.31 Å	2.14 Å	2.30 Å	2.30 Å	2.30 Å	2.30 Å
Ch–M–Cl	109°	108°	108°	109°	108°	109°	110°	110°
ν_{MCh}^b	1286	1143	1132	712	629	592	392	296
k_{MCh}^b	11.86	10.50	11.10	5.86	5.55	5.61	5.02	3.91

^a All complexes are C_{3v} minima as shown below. ^b Intrinsic stretching frequencies (ν_{MCh} , in cm⁻¹) and MCh force constants (k_{MCh} , in mdyn Å⁻¹) are calculated using the method of Boatz and Gordon.²⁰



that we will return to once more metric data has been collected.

Two of the more interesting oxos which have been recently characterized both possess the MX₃O motif—d⁴-tris(mesityl)-Ir^V-oxo²¹ and d⁴-bis(acetylene)Re^{III}-oxo complexes (**B**).⁴⁵ The former is the first structurally characterized Ir-oxo complex.⁴⁶ Mayer has presented a qualitative molecular orbital analysis of pseudotetrahedral ReO complexes in order to understand their ability to stabilize low formal oxidation state.⁴⁵ The complex IrMes₃O is ≈ C₃ with mesityls forming a three-bladed propeller; the lowest energy C₃ structure, **3**, of a IrMe₃O model has a calculated IrO



bond length of 1.70 Å in very good agreement with experiment,²¹ IrO = 1.725(9) Å; calculated Ir–C bonds = 2.04 Å in **3** and range from 2.00 to 2.03 Å in IrMes₃O.²¹ We have previously compared ECP results for [Re(O)(acetylene)₂(H)] with [Re(O)(2-butyne)₂(I)];²² the calculated Re–oxo bond length is 1.71 Å, comparing favorably with an experimental bond length of 1.745(7) Å.⁴⁷ The ability of ECPs to predict the structure of these low-valent oxo complexes, in addition to the more common high-valent examples, is encouraging and highlights the need for a flexible scheme to address the wide diversity in TM chemistry.

iii. M(X)₄(Ch) Complexes. Complexes of the type MX₄Ch almost invariably assume a square-pyramidal geometry, particularly for simple unidentate ligands,^{2,47–62} allowing Ch to occupy

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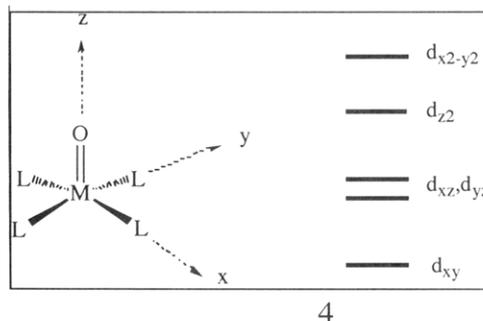
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the apical position in the square pyramid and effectively π -bond to both of the perpendicular metal d π orbitals which are vacant in the high-valent complexes which typify this family. Examples of the MX₄Ch structural motif are known for the Ti- through Fe-triads with d orbital occupancies of 0, 1, and 2.² A notable counterexample is the d⁴ complex of Mayer et al., [Re(O)(2-butyne)₂(bipy)]⁺,⁴⁷

Comparison of anionic d¹ and neutral d⁰ MOX₄ analogues (M = Cr, Mo, W) affords an opportunity to probe oxidation state effects on TMCh multiple bonding and to study the qualitative bonding schemes forwarded for these complexes. The d orbital splitting diagram of MOX₄, **4**, is



similar to that for MOX₅⁶³ since orbitals derived from the octahedral t_{2g} set (d_{xz}, d_{yz}, d_{xy} in **4**) are little affected by removal of a trans ligand. The unpaired electron in d¹-MOX₄ should reside in a metal-based, nonbonding orbital. If the MO vector is the z-axis and MX bonds lie in the xz and yz planes, **4**, the ground state for d¹-MOX₄ should have one electron in d_{xy} (²B₂). Addition of an electron into d_{xy} should increase MX bond lengths since this orbital is metal d π -halide p π antibonding. The ECP calculations support these conclusions. All d⁰ and d¹ MOX₄ complexes described below are C_{4v} minima with ²B₂ ground states for the latter, Table 3. Increases in MX bond lengths are the most noticeable perturbation upon going from d⁰-MOX₄ to d¹-[MOX₄]⁻. Finally, there are small changes in the metal–oxo linkage; metal–oxo bond lengths are slightly longer in d¹ anions than d⁰ neutrals as expected given the lower oxidation state of the former.

In general, agreement between calculated and experimental^{48–51} geometries is excellent for C_{4v} MOX₄⁻ complexes of the Cr-triad. Metal–oxo bonds tend to be too short by only 1–3%, while metal–

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Table 3. MOX₄ Complexes^a

	Cr/F	Cr/Cl	Cr/Br	Mo/F	Mo/Cl	Mo/Br	W/F	W/Cl	W/Br
<i>d</i> ⁰ Neutral MOX ₄ Complexes of Cr-Triad									
M–O	1.46 Å	1.47 Å	1.47 Å	1.61 Å	1.61 Å	1.61 Å	1.64 Å	1.63 Å	1.63 Å
M–X	1.71 Å	2.21 Å	2.42 Å	1.84 Å	2.32 Å	2.48 Å	1.84 Å	2.32 Å	2.48 Å
O–M–X	105°	106°	107°	105°	105°	104°	105°	104°	104°
ν_{MO}^b	1370	1355	1343	1229	1219	1207	1212	1215	1207
k_{MO}^b	13.53	13.23	13.00	12.24	12.04	11.81	12.74	12.81	12.64
<i>d</i> ¹ Anionic MOX ₄ Complexes of Cr-Triad ^c									
M–O	1.49 Å	1.47 Å	1.64 Å	1.62 Å	1.62 Å	1.67 Å	1.64 Å	1.64 Å	1.64 Å
M–X	1.78 Å	2.27 Å	2.44 Å	1.93 Å	2.41 Å	2.56 Å	1.93 Å	2.41 Å	2.57 Å
O–M–X	106°	104°	104°	108°	105°	105°	108°	105°	105°
ν_{MO}^b	1282	1321	1315	1141	1181	1179	1121	1171	1168
k_{MO}^b	11.85	12.57	12.46	10.55	11.30	11.25	10.90	11.88	11.83
Anionic and Neutral MX ₄ O Complexes									
	Ti/Cl/–2	V/Br/–1	Tc/Cl/–1	Re/Cl/–1	Re/F/0	Re/Cl/0	Os/F/0	Os/Cl/0	
M–O	1.58 Å	1.50 Å	1.59 Å	1.62 Å	1.61 Å	1.61 Å	1.59 Å	1.59 Å	
M–X	2.49 Å	2.46 Å	2.37 Å	2.39 Å	1.84 Å	2.31 Å	1.85 Å	2.30 Å	
O–M–X	104°	103°	106°	106°	108°	106°	110°	108°	
ν_{MO}^b	1133	1268	1224	1219	1257	1247	1289	1263	
k_{MO}^b	9.07	11.53	12.12	12.89	13.72	13.49	14.46	13.88	

^a Column headings are of the form M/X/q; M is the transition metal; X is the halide ligand; q is the overall charge on the complex. The complexes are all C_{4v} minima as shown below. ^b Intrinsic stretching frequencies (ν_{MCh} , in cm⁻¹) and MCh force constants (k_{MCh} , in mdyn Å⁻¹) are calculated using the method of Boatz and Gordon.²⁰



halide bond lengths are too high by a similar small percentage; oxo–metal–halide bond angles are in the range 105 ± 3°, as are experimental values. For WOCl₄⁻ the calculated WO bond length is 1.64 Å in very good agreement with data⁴⁸ for [WOCl₄]⁻[PPh₄]⁺, 1.676(7) Å, and only 0.01 Å longer than the calculated WO bond length in WOCl₄, Table 3. The calculated CrO bond length in the C_{4v} minimum of CrOCl₄⁻ is 1.47 Å, in good agreement with the experimental value of 1.519(12) Å for the [AsPh₄]⁺ salt of CrOCl₄⁻.⁴⁹ Note that calculated CrO bond lengths are essentially identical (and the intrinsic stretching frequency for CrO bonds shift by only 34 cm⁻¹) for the *d*⁰ neutral and *d*¹ anion, as expected from the simple bonding model⁶³ outlined above for MOX₄ complexes, 4. The salts [MoOCl₄]⁻[AsPh₄]⁺ and [MoOBr₄]⁻[PPh₄]⁺ have reported MoO bond lengths of 1.610(10)⁵⁰ and 1.726(14) Å.⁵¹ Calculated MoO values are 1.62 Å for both tetra(chloro) and tetra(bromo) analogues. The wide variance in oxo complexes has been well studied in connection with distortional isomerism, and the above examples have been quoted in support of this phenomenon.⁶⁴ Recent computations by Song and Hall⁶⁵ and experiments by Parkin⁶⁶ and Desrochers et al.⁶⁷ have called distortional isomerism into question. We find no evidence for stable, long bond isomers in any five-coordinate, oxyhalides of the Cr-triad.

Several anionic and neutral MOX₄ complexes have been structurally characterized where M is not of the Cr-triad.^{52–55,60–62} Ground-state structures are C_{4v} in computational and experimental models, Table 3. We have previously discussed the good agreement between theory and experiment²² for ReOCl₄⁻ (C). The metric data for VOBr₄⁻ is VO = 1.50 Å (1.552(9) Å, experimental), VBr = 2.46 Å (2.412(1) Å, experimental), and OVBr = 103° (103.1(1)°).⁵³ Note that the calculated TiO bond length in TiOCl₄²⁻ is 1.58 Å, in line with data for other titanyl complexes (*vide supra*),^{30–34} but significantly shorter than the reported Ti–oxo bond length in the bis(NEt₄)⁺ salt of TiOCl₄²⁻.⁵² The cause for the discrepancy among the calculations, X-ray data for other titanyl complexes,^{30–36} and the crystal structure⁵² of [NEt₄]₂⁺[TiOCl₄]₂²⁻ is unclear. Cotton et al.⁵⁴ have characterized the PPN⁺ salt of TcOCl₄⁻ which shows good agreement with calculations: TcO = 1.59 Å (1.610(4) Å), TcCl = 2.37 Å (2.291(1) Å–2.317(2) Å, av = 2.31 Å), and OTcCl = 106° (103.0(2)–111.5(3)°, av = 107°). The calculated structure for OsOCl₄

has OsO = 1.59 Å, OsCl = 2.30 Å, and OOsCl = 108° in reasonable agreement with gas-phase electron diffraction studies:⁶⁰ OsO = 1.663(9) Å, OsCl = 2.358(5) Å and OOsCl = 108.3(4)°. The complex OsOMe₄ is a rare case of a stable, high-valent organometallic oxide.⁶² Calculated and experimentally determined (by electron diffraction) metric data show excellent correspondence: OsO = 1.681(1) Å (1.64 Å, calcd), OsC = 2.096(3) Å (2.11 Å, calcd), OOsC = 112.2(5)° (113°, calcd), COsC = 81.8(4)° (81°, calcd).⁶²

Recent electron diffraction (ED) studies of neutral MX₄Ch complexes provide another good opportunity to investigate the flexibility of the ECP approach for a series of chalcogens.^{2,14} For *d*⁰, group VIB oxos, MOX₄, calculated metal–oxo bond lengths for C_{4v} minima show minimal change as a function of halide ligand: CrO = 1.46 Å (CrOF₄), 1.47 Å (CrOBr₄ and CrOCl₄); MoO = 1.61 Å (MoOF₄, MoOCl₄, and MoOBr₄); WO = 1.64 Å (WOF₄) and 1.63 Å (WOCl₄ and WOBr₄). Calculated metal–oxo bond lengths compare very well with data from electron diffraction: MoO = 1.650(3) Å (MoOF₄),⁵⁷ MoO = 1.658(2) Å (MoOCl₄),⁵⁶ WO = 1.666(4) Å (WOF₄),⁵⁹ WO = 1.684(4) Å (WOCl₄),⁵⁹ and WO = 1.684(3) Å (WOBr₄).⁵⁹ The entire series of complexes WX₄Ch has been characterized by ED for X = F, Cl, Br, Ch = O, S, Se.¹⁴ Calculated and experimental data for these WX₄Ch complexes are collected in Table 4 along with calculated values for the as yet unsynthesized telluridos. The WCh bond distances in WCl₄Ch, Table 4, relative to the oxo are WS–WO = 0.44 Å (0.42 Å, experimental); WSe–WO = 0.54 Å (0.51 Å, experimental), and WTe–WO = 0.77 Å, showing good reproduction of experimental trends.¹⁴ Differences in bond lengths relative to the oxo analogue are closer to those found for Cl₃TaCh than Cp₂ZrCh. In terms of absolute predictions there is very good agreement for MCh, MX, and ChMX metric data; MCh bonds tend to be short by only 2–3%, and MX bond lengths are long by a few percent on average. Thus, as found for group IVB metallocenes and Ta there is consistently good agreement between experiment and ECP calculated geometries for a continuous series of chalcogens.

iv. M(X)₅(O) Complexes. Six-coordinate oxos based on the octahedral geometry have been widely studied.² The X₅ ligand set can be anything from a porphyrin ring with an axial ligand to five unidentate halides or a wide variety of neutral Lewis

Table 4. WCl_4Ch Complexes

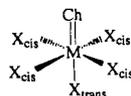
	MCh _{calc}	MCh _{expt}	MX _{calc}	MX _{expt}	ChMX _{calc}	ChMX _{expt}	ν_{MCh}	k_{MCh}
WF ₄ O	1.64 Å	1.67 Å	1.84 Å	1.85 Å	105°	105°	1212	12.74
WCl ₄ O	1.63 Å	1.69 Å	2.32 Å	2.28 Å	104°	102°	1215	12.81
WBr ₄ O	1.63 Å	1.68 Å	2.48 Å	2.44 Å	104°	103°	1200	12.51
WF ₄ S	2.05 Å	2.10 Å	1.84 Å	1.85 Å	106°	105°	625	6.26
WCl ₄ S	2.07 Å	2.11 Å	2.32 Å	2.28 Å	102°	104°	638	6.53
WBr ₄ S	2.05 Å	2.11 Å	2.48 Å	2.43 Å	105°	104°	632	6.40
WF ₄ Se	2.20 Å	2.23 Å	1.84 Å	1.85 Å	106°	105°	406	5.41
WCl ₄ Se	2.17 Å	2.20 Å	2.33 Å	2.28 Å	105°	104°	419	5.76
WBr ₄ Se	2.18 Å	2.22 Å	2.48 Å	2.43 Å	105°	103°	414	5.63
WF ₄ Te	2.40 Å	NA ^b	1.84 Å	NA	106°	NA	289	3.75
WCl ₄ Te	2.40 Å	NA	2.33 Å	NA	105°	NA	309	4.29
WBr ₄ Te	2.40 Å	NA	2.48 Å	NA	105°	NA	305	4.19

^a Experimental data for these complexes are taken from ref 14; all complexes are C_{4v} minima. ^b NA = not available.

Table 5. MOX_5 Complexes^a

	V/F/-2	V/Cl/-2	Nb/F/-2	Nb/Cl/-2	Cr/Cl/-2	Mo/F/-2	Mo/Cl/-2	Mo/Br/-2	W/Cl/-2	W/Br/-2
M-O	1.55 Å	1.51 Å	1.73 Å	1.67 Å	1.48 Å	1.68 Å	1.63 Å	1.63 Å	1.66 Å	1.65 Å
M-X _{cis}	1.85 Å	2.36 Å	1.99 Å	2.55 Å	2.36 Å	1.99 Å	2.49 Å	2.65 Å	2.49 Å	2.65 Å
M-X _{trans}	1.98 Å	2.67 Å	2.11 Å	2.70 Å	2.55 Å	2.05 Å	2.63 Å	2.895 Å	2.62 Å	2.83 Å
O-M-X _{cis}	95°	94°	94°	94°	93°	95°	93°	93°	94°	93°
ν_{MO}^b	1148	1237	990	1089	1283	1067	1149	1155	1143	1149
k_{MO}^b	9.46	10.98	7.88	9.54	11.86	9.22	10.69	10.81	11.32	11.45

^a Column headings are of the form M/X/q; M is the transition metal; X is the halide ligand; q is the overall charge on the complex. The complexes are all C_{4v} minima as shown below. Group VIB complexes have a 2B_2 ground state and were calculated using a restricted open-shell Hartree-Fock (ROHF) wave function. ^b Intrinsic stretching frequencies (ν_{MCh} , in cm^{-1}) and MCh force constants (k_{MCh} , in $mdyn \text{ \AA}^{-1}$) are calculated using the method of Boatz and Gordon.²⁰



bases.²⁻⁴ The interesting story of distortional isomerism has led to interest in the MX_5O motif.⁶⁴⁻⁶⁷ Below we consider a small sample of C_{4v} MX_5O complexes for which vibrational data has been published.²⁻⁴ The prevalence of d orbital occupancies of 0, 1, and 2 in MX_5O complexes is explained by the classic Ballhausen-Gray analysis⁶³ which is very similar to the bonding picture given in 4. Two orbitals in the t_{2g} set of octahedral complexes are perturbed to higher energy by the π -donor ability of the oxo, leaving a low-energy, nonbonding d orbital (d_{xy} if the MO vector is the z-axis) which can hold either 0, 1, or 2 electrons. Complexes with d populations greater than 2 must populate orbitals which are metal $d\pi-O\pi$ antibonding, thus contributing to instability of the complex. The few examples of MX_5O complexes with d orbital occupancies of greater than 2 such as Meyer's d^4 -Ru(IV)-oxo polypyridyl⁶⁸ and the putative Fe(V)-oxo active species in cytochrome P-450⁷ are highly reactive intermediates.

The MOX_5 complexes in Table 5 are C_{4v} minima. As expected, addition of a halide trans to the oxo lengthens the metal-oxo bond in MOX_5 , Table 5, versus that in MOX_4 for Cr-triad metals,

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(64) Other examples purporting to show distortional isomerism are collected in Table 5.1 of ref 2, p 153. A statistical analysis of reported metal-oxo bond lengths, and the relation of metal-oxo bond lengths in "bond stretched isomers" to the majority of L_nMO complexes is given: Mayer, J. M. *Inorg. Chem.* **1988**, *27*, 3899.

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Table 3. The d^1 MOX_5 complexes have a 2B_2 ground state.⁶³ A comparison between calculated and experimental $ReOF_5$ structures is given elsewhere.²² Calculated metal-oxo bond lengths in VF_5O^{2-} and VCl_5O^{2-} are 1.55 and 1.51 Å, respectively, in very good agreement with $VO = 1.54(1)$ Å in $[VF_5O]^{2-}[enH_2]^{+2}$.⁶⁹ The VF_{cis} bond lengths of 1.85 Å concur with average crystal structure values ($VF_{cis} = 1.80$ Å);⁶⁹ the calculated VF_{trans} bond is 1.98 Å, longer than VF_{cis} , but 0.12 Å (6%) shorter than VF_{trans} in $[VF_5O]^{2-}[enH_2]^{+2}$.⁶⁹ The salt $K_2MoOF_5 \cdot H_2O$ has been characterized:⁷⁰ $MoO = 1.66(2)$ Å (1.68 Å, calcd), $MoF_{cis}(av) = 1.88$ Å (1.99 Å, calcd), $MoF_{trans} = 2.03$ Å (2.05 Å, calcd), $OMoF_{cis}(av) = 94^\circ$ (95, calcd). The complex NbF_5O^{2-} has an NbO bond length of 1.73 Å, in good agreement with the crystallographically determined value of 1.75(2) Å.⁷⁰ Interestingly, the closely related complex $NbCl_5O^{2-}$ has a calculated NbO bond length which is shorter than the pentafluoro analogue (a similar trend to that found in the previous V^{+5} complexes), while the crystal structure⁷¹ of $[NbCl_5O]^{2-}[AsPh_4]^{+2}$ puts the NbO bond length in $[NbF_5O]^{2-}[N_2H_6]^{2+}$ at 1.967(6) Å⁷⁰ or roughly 0.2 Å longer than the NbO bond in pentafluoro dianion! It is uncertain to what extent these differences are due to distortional isomerism⁶⁴⁻⁶⁷ and to what extent this is a reflection of differences in the trans influence of halides.

b. $L_nM(Ch)_2$. Dioxo complexes and heavier analogues are general four or six coordinate.² Dichalcogenido complexes have been reported for the V-, Cr-, Mn-, and Fe-triads. In MX_2Ch_2 the metal is typically from the Cr-triad, although d^1 $Re(O)_2(Mes)_2$,⁷² d^2 $Os(O)_2(Mes)_2$,⁷² and d^0 $Os(O)_2(N-t-Bu)_2$ ⁷³ have been reported. Dioxo complexes have seen much interest in connection with their ability to oxidize organic substrates, using O_2 as an

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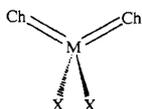
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Table 6. $M(O)_2(X)_2$ Complexes^a

	Cr/F	Cr/Cl	Cr/Br	Mo/F	Mo/Cl	Mo/Br	W/F	W/Cl	W/Br
M–O	1.50 Å	1.50 Å	1.50 Å	1.65 Å	1.64 Å	1.64 Å	1.67 Å	1.66 Å	1.66 Å
M–X	1.70 Å	2.12 Å	2.28 Å	1.85 Å	2.29 Å	2.43 Å	1.84 Å	2.29 Å	2.43 Å
O–M–O	109°	109°	110°	107°	107°	107°	108°	107°	107°
X–M–X	109°	111°	111°	110°	111°	112°	111°	113°	113°
ν_{MO}^b	1261	1238	1223	1149	1138	1131	1142	1140	1134
k_{MO}^b	11.46	11.04	10.78	10.69	10.49	10.36	11.30	11.27	11.14

W(Ch)(Ch')(Cl) ₂ Complexes ^c						
	O/O	O/S	O/Se	S/S	S/Se	Se/Se
W–Ch	1.66 Å	1.65 Å	1.65 Å	2.09 Å	2.09 Å	2.21 Å
W–Ch'	2.29 Å	2.11 Å	2.23 Å	2.09 Å	2.21 Å	2.21 Å
Ch–W–Ch'	107°	108°	108°	109°	109°	110°
ν_{MCh}^b	1140	1160	1161	593	597	386
k_{MCh}^b	11.27	11.66	11.68	5.65	5.72	4.90
ν_{MCh}^b		586	379		386	
k_{MCh}^b		5.52	4.72		4.90	

^a Complexes of the type $M(X)_2(Ch)(Ch')$ are C_{2v} ($Ch = Ch'$) and C_2 ($Ch \neq Ch'$) minima as shown below. ^b Intrinsic stretching frequencies (ν_{MCh} , in cm^{-1}) and MCh force constants (k_{MCh} , in $mdyn \text{ \AA}^{-1}$) are calculated using the method of Boatz and Gordon.²⁰ ^c For cases in which $Ch \neq Ch'$, Ch is the lighter chalcogenide.



oxygen source.^{74–76} *trans*-Dichalcogenido W(IV) complexes $(W(L)_4(Ch)_2)$, L = neutral ligand (PMe_3 or isocyanide)) have been synthesized for $(Ch)_2 = (S)_2$,⁷⁷ $(Se)_2$,⁷⁸ $(Te)_2$,¹¹ $(S)(Se)$,⁷⁸ and $(Se)(Te)$,⁷⁸ with mixed chalcogenidos as not yet structurally characterized. A mixed bis(chalcogenido) complex $Mo^{IV}(dppe)_2(O)(S)$ has been reported.⁷⁹ The general preference of d^0 and d^2 $L_4M(Ch)_2$ complexes for *cis* and *trans*, respectively, arrangements of the chalcogenides has been explained in terms of less competition among the $p\pi$ orbitals of the Ch ligands for vacant $d\pi$ orbitals in the former and the presence of a metal nonbonding orbital to accept the two d electrons in the latter.⁴

MCh₂X₂ Complexes. Calculated MX_2O_2 minima are C_{2v} .² The calculated minimum in chromyl chloride has $CrO = 1.50 \text{ \AA}$ (1.57(3), experimental), $CrCl = 2.12 \text{ \AA}$ (2.12(3) Å), $OCrO = 109^\circ$ (105(4)°), and $ClCrCl = 109^\circ$ (113(3)°),³⁷ Table 6. $Cr(O)_2(OC_{15}H_{25})_2$ has reported Cr–oxo bond lengths of 1.57(1) Å and an oxo–Cr–oxo bond angle of 107.2(8)°;⁸⁰ the bond length is clearly closer to electron diffraction results.³⁷ The complex $Cr(O)_2(OSiPh_3)_2$ shows two inequivalent Cr–oxo bonds: (1.514(13) Å (closer to the calculated value) and 1.568(12) Å (closer to the ED result)).⁸¹ Fortunately, a more recent ED study of chromyl chloride has been published;⁸² newer data are consistent with Palmer³⁷ except that $OCrO$ is larger in the newer study (108.5(4)°), hence closer to the calculated value, Table 6. French et al.⁸³ have reported an ED study of CrO_2F_2 and here again the calculated CrO bond length is 1.50 Å, 5% shorter than experiment (1.575(2) Å), while other calculated metric data are in excellent agreement with experiment. Based on studies of TM multiple bonding¹⁵ it is found that for a given family of compounds the importance of electron correlation increases as one goes from right to left in the transition series and from heavier to lighter members of a triad.

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Metal–oxo bond lengths in molybdenyl and tungstenyl halides are roughly 0.03–0.05 Å shorter (≈ 2 –3%) than found in complexes in which two additional neutral bases have been coordinated. For example, Mo and $W(O)_2(Cl)_2(OPPh_3)_2$ have metal–oxo bond lengths of 1.673(1) Å, 1.695(1) Å (Mo) and 1.702(9) Å, 1.706(8) Å (W),² compared to $MoO_{calcd} = 1.64 \text{ \AA}$ for MoO_2Cl_2 and $WO_{calcd} = 1.66 \text{ \AA}$ for WO_2Cl_2 , Table 6. Computations and experiments^{80–83} show near tetrahedral angles about the TM for the d^0 group VIB complexes, Table 6.

Research from the Wilkinson lab⁷² has produced an interesting pair of dioxos: d^1 $Re(O)_2(Mes)_2$ and d^2 $Os(O)_2(Mes)_2$. Angles about the TM in $Os(O)_2(Mes)_2$ deviate markedly from tetrahedral values;⁷² the O–Os–O angle is significantly expanded to 136.1(3)°, while the C–Os–C angle is markedly compressed (96.0(3)°) despite the bulk of the mesityls.⁷² Simple MO_2Cl_2 models were investigated with ECP methods. For the series of MO_2Cl_2 complexes (M = W, Re, Os) metal–oxo and metal–chloro bond lengths stay nearly constant at 1.66 and 2.29 Å, respectively, consistent with structural data for d^1 Re and d^2 $Os(O)_2(Mes)_2$, i.e., M–O and M–Cl bond lengths are roughly equivalent at 1.69 and 2.05 Å, respectively.⁷² Calculated oxo–metal–oxo bond angles reproduce the experimental trend of increasing OMO angle with increasing d orbital occupation: $OMO = 107^\circ$ (W), 117° (Re), 121.5(4)°, experimental) and 127° (136.1(3)°).⁷² Likewise, the Cl–M–Cl angles decrease in a similar manner to the C–M–C bonds in MO_2Mes_2 : Cl–M–Cl = 113° (W), 98° (Re), and 91° (Os). Keeping MO and MCl bond lengths equal and distorting to tetrahedral angles requires only 2–3 kcal mol^{-1} at the RHF level for the Re^{VI} and Os^{VI} complexes. That the observed geometric distortions are reproduced in simple model calculations is consistent with a subtle electronic effect giving rise to angular distortions, and further evidence that ECP methods are adequately describing the electronic structure of these complexes.

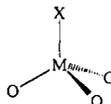
Gibson et al.⁸⁴ have developed synthetic routes to MX_2Ch_2 complexes for Ch = S, including mixed chalcogenides such as $Mo(O)(S)Cl_2$.⁸⁴ The bis(sulfido) and sulfido(oxo) complexes of $MoCl_2$ and WCl_2 have been synthesized, although no metric data has been reported.⁸⁴ We have chosen examples for the metal W ($WCl_2Ch(Ch')$ Ch, $Ch' = O, S, Se$) in order to probe the consequences of competition for $d\pi$ – $p\pi$ bonding between *cis*-chalcogenido ligands, Table 6. As expected, there is a weakening of WS and WSe bonds when the strongly π -bonding oxo ligand

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Table 7. XMO₃ Complexes^a

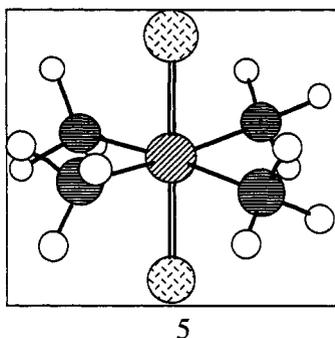
	CrO ₃ Cl ⁻	CrO ₃ F ⁻	MoO ₃ Cl ⁻	MnO ₃ F	TcO ₃ F	ReO ₃ Me	ReO ₃ F	ReO ₃ Cl	ReO ₃ Br	OsO ₃ N ⁻
M-O	1.55 Å	1.55 Å	2.40 Å	1.51 Å	1.64 Å	1.67 Å	1.66 Å	1.66 Å	1.66 Å	1.73 Å
M-X	2.25 Å	1.78 Å	1.70 Å	1.72 Å	1.84 Å	2.12 Å	1.84 Å	2.28 Å	2.42 Å	1.63 Å
O-M-X	107°	108°	108°	106°	108°	103°	109°	108°	108°	108°
ν_{MO}^b	1125	1113	1023	997	1127	1112	1142	1134	1131	944
k_{MO}^b	9.12	8.92	8.47	7.26	10.28	10.73	11.31	11.17	11.1	7.75

^a All complexes are d⁰ C_{3v} minima as shown below. ^b Intrinsic stretching frequencies (ν_{MCh} , in cm⁻¹) and MCh force constants (k_{MCh} , in mdyn Å⁻¹) are calculated using the method of Boatz and Gordon.²⁰



is introduced. For example, WSe bond lengths in WCl₂Se₂ are 2.21 Å with a force constant of 4.90 mdyn Å⁻¹; replacement of selenido (which is expected to be the weakest π -bonding ligand in the set) with oxo causes the WSe bond to stretch by 0.02 Å, and the force constant is reduced to 4.72 mdyn Å⁻¹ (corresponding to a 7 cm⁻¹ change in the intrinsic stretching frequency). However, these changes are very small suggesting that competition between Ch and Ch' bonds for metal d π -ligand p π bonding in these pseudo-tetrahedral complexes is very small.

Geometries for D_{2d} minima of W(Ch)₂(PH₃)₄ models (Ch = O, S, Se, Te) were optimized with ECP methods on parallel supercomputers to compare with recent data^{11,77,78} and to study the *trans*-bis(chalcogenides) arrangement. A model of the first structurally characterized terminal tellurido, W(Te)₂(PH₃)₄ **5**, shows excellent agreement with experiment for W(Te)₂(PMe₃)₄,¹¹ in



particular for the WTe₂ core:¹¹ WTe = 2.61 Å (2.596(1) Å); WP = 2.57 Å (2.508(2) Å); TeWTe = 180° (180°); TeWP = 87° and 93° (82.1(1)° and 97.9(1)°); PWP = 90° and 175° (91.1(1)° and 164.2(1)°). The biggest differences are in angles involving the phosphine ligand which is understandable given the difference in the bulk of PH₃ model and PMe₃.¹¹ The bis(selenido) and bis(sulfido) models of **5** have WSe = 2.38 and WS = 2.26 Å, in excellent agreement with experiment: WSe = 2.38 Å⁷⁸ and WS = 2.248(2).⁷⁷ *trans*-W(PH₃)₄(O)₂ has a calculated WO bond length of 1.80 Å; a bis(oxo) member of the WL₄Ch₂ series (L = neutral base) has not been reported, but a d²-*trans*(dioxo) Mo complex, NaK₃[Mo(O)₂(CN)₄], has been characterized.⁸⁵ Analogous bond lengths involving Mo and W are expected to be similar due to the lanthanide contraction. The *trans*-dioxo-Mo(IV) complex has MoO = 1.834(9) Å, longer by about 0.1 Å than the typical MoO bond lengths in d⁰-*cis*(dioxo) Mo complexes, in reasonable accord with the calculated value for W(PH₃)₄(O)₂.² The mixed sulfido-oxo complex Mo(dppe)₂(O)(S) is of interest for several reasons, not the least of which is the fact that the complex contains an equivalent of sulfuric acid and sulfur dioxide in the unit cell.⁷⁹ An ECP optimization of W(O)(S)(PH₃)₄ shows very good agreement with the reported structure: WO = 1.73

Å (MoO = 1.77(1) Å⁷⁹), and WS = 2.37 Å (MoS = 2.415(7) Å⁷⁹). Calculations show the WO bond in the sulfido oxo to be shorter than in the *trans*-dioxo case and the WS bond to be shorter in the *trans*-bis(sulfido), results pointing to a stronger *trans* effect for O²⁻ versus S²⁻.

c. L_nM(Ch)₃ Complexes. The trioxo moiety is generally observed to be nonplanar in those complexes in which it appears.⁴ Barium ruthenate, BaRu(O)₃(OH)₂ is deviant from the norm possessing a planar trioxo moiety in the equatorial plane of a trigonal bipyramid.⁴ Herrmann et al. have recently developed the chemistry of the ReO₃ functionality;⁸⁶ applications such as olefin metathesis^{86a} and epoxidation^{86b} catalysts have been reported. X is typically unidentate although Cp'ReO₃ has been structurally characterized.⁸⁷ Oxo-bridged species such as dichromate (Cr₂O₇²⁻),⁸⁸ dimolybdate (Mo₂O₇²⁻),⁸⁹ and Re₂O₇⁹⁰ can also be considered as trioxo complexes. Trichalcogenido moieties for the heavier chalcogens are rare. Examples of which we are aware are [CpTa(S)₃]²⁻ (terminal sulfidos interact strongly with solvated Li⁺),⁹¹ [CpW(S)₃]⁻,⁹² and MeCp(dppe)RuSRe(S)₃.⁹³

The structures of ReO₃F, ReO₃Cl, and MnO₃F have been studied by microwave spectroscopy.⁹⁴ As expected, there is greater discrepancy between experiment and the RHF geometry (in parentheses) for the complex involving a first-row TM: MnO = 1.586(5) Å (1.51 Å), MnF = 1.724(5) Å (1.72 Å), and OMnF = 108.5(1)° (106°), suggesting that for highly accurate work an account of electron correlation may be desirable for MnO₃F. The ReO bond lengths are 1.692(3) and 1.702(3) Å for the fluoro and chloro complexes,⁹⁴ respectively, in very good agreement with calculated values of 1.66 Å, Table 7. Likewise, calculated and experimental Re-halide and oxo-Re-halide angles show close correspondence: ReF = 1.859(8) Å (1.84 Å, calcd), ReCl = 2.229(4) Å (2.28 Å, calcd), OReF = 109.5(3)° (109°, calcd), and OReCl = 109.3(1)° (108°, calcd).⁹⁴ The Cs salt of OsO₃N⁻ possesses OsO bond lengths of \approx 1.74 Å and an OsN bond length of 1.676(15) Å, in agreement with calculation OsO = 1.73 and OsN = 1.63 Å.⁹⁵

Given the paucity of structurally characterized tris(chalcogenido) complexes for heavier chalcogens we undertook a model study of the anion in [Cp*W(S)₃]⁻[NEt₃H]⁺, **6**.⁹² Analysis of

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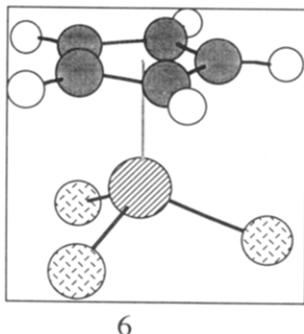
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6 can be compared with the isostructural CpReO_3 .⁸⁷ The complexes are C_s minima although local C_{3v} symmetry of the MCh_3 fragment is apparent. The distance from the Cp centroid to W is 2.13 Å (2.20 Å, calcd); the average Re–C distance in Cp^+ReO_3 is 2.40 Å (2.46 Å, calcd). The centroid–WS angles average 113° in the experimental⁹² and computational models. The OREO angles are 106° (av⁹⁷) and $\text{ReO} = 1.70$ Å (av⁹⁷) in Cp^+ReO_3 compared with 105° and 1.68 Å, respectively, in the model. Average WS bond lengths are 2.19 Å (experimental⁹²) and 2.20 Å (calcd). Thus, agreement between ECP results and experimental data is excellent for this rare example of a tris-(chalcogenide) moiety incorporating a heavier chalcogenide and the lighter trioxo analogue.

d. $\text{M}(\text{Ch})_4$ Complexes. The d^0 metalates and heavier congeners, $[\text{M}(\text{Ch})_4]^{q-}$, constitute the best studied, computationally and experimentally, class of terminal chalcogenido complexes.²⁻⁴ Ubiquitous salts such as potassium permanganate² were “well-known to chemists in the early nineteenth century”, while synthesis of thiometalates by introduction of H_2S into acidic solutions of molybdate and tungstate was reported by Berzelius as early as 1826.^{5a} Some of the earliest computational studies of TM complexes are the studies of tetrahedral $[\text{MO}_4]^{q-}$ complexes by Wolfsberg and Helmholtz⁹⁶ employing a predecessor of the extended Hückel method. The greatest amount of data exists for homoleptic $[\text{M}(\text{Ch})_4]^{q-}$ complexes in which Ch = O and S,^{2-5,97} although some $[\text{M}(\text{Se})_4]^{q-}$ complexes have been recently characterized.^{98,99} Mixed metalates, $[\text{M}(\text{O})_x(\text{S})_{4-x}]^{q-}$, $[\text{M}(\text{O})_x(\text{Se})_{4-x}]^{q-}$, and $[\text{M}(\text{S})(\text{Se})_{4-x}]^{q-}$, are known for $\text{M} = \text{V}, \text{Mo}, \text{W}$ and Re .⁵

Geometry optimized ground states for homoleptic $[\text{M}(\text{Ch})_4]^{q-}$ complexes are tetrahedral, Table 8. In general, there is excellent agreement between theory and experiment for metalates and tetrathiometalates. For the ten metalates for which there is experimental data,^{2,3} Table 8, the average error in metal–oxo bond lengths is less than 2%. Similarly, good agreement is found between ECP predicted geometries and experiment⁵ for tetrathiometalates, Table 8. A word of caution is in order regarding the tetrathiometalates of the first row metals, $[\text{Cr}(\text{S})_4]^{2-}$ and $[\text{Mn}(\text{S})_4]^-$, since it is observed¹⁵ that for a family of related TM complexes the appropriateness of single-determinant wave functions tends to decrease as one goes toward the right in the first transition series. Also, the weakening of $\text{M } d\pi\text{--Ch } p\pi$ bonding for heavier MG elements can exacerbate the electron correlation problem. However, for the five tetrathiometalates with which one can compare experimental and calculated metric data for metal–sulfido bond lengths,^{5,97} the average difference between theory and experiment is less than 2%.

Tetraselenometalates have recently succumbed to crystallographic analysis.^{98,99} NbSe_4^{3-} and TaSe_4^{3-} have calculated metal–selenido bond lengths of 2.46 Å, $\approx 3\%$ longer than the experimental

average, Table 8.⁹⁹ Agreement with crystal data is better for group VIB dianions, 1–2%, Table 8.⁹⁸ Finally, we have calculated the structure of $\text{Td } \text{WTe}_4^{2-}$; $\text{WTe} = 2.57$ Å, or 0.23 Å longer than WSe in WSe_4^{2-} , similar to that found, experimentally and computationally, for other Se/Te congeners (*vide supra*). The structure of a tetratellurometalate has, to our knowledge, not been reported although given the rapid progress in this area it will not be surprising to see one in the near future. If calculations on lighter metalates are an indication, one can expect the ECP predicted geometry to be in good agreement with this interesting synthetic target.

Mixed thiometalates, $[\text{M}(\text{O})_x(\text{S})_{4-x}]^{q-}$ have C_{3v} ($x = 1, 3$) and C_{2v} ($x = 2$) minima. Mixed tetrathiometalates, Table 9, show MO bonds to shorten as oxos are replaced with sulfidos, as expected since oxo is a stronger π -bonding ligand than sulfido. However, calculations show the degree of shortening in metal–oxo bond lengths changes as the metal changes. For V complexes ($[\text{V}(\text{O})_x(\text{S})_{4-x}]^{2-}$) incrementally replacing an oxo with a sulfido causes the metal–oxo bond to shorten by 0.04; for $[\text{Re}(\text{O})_x(\text{S})_{4-x}]^-$ systems the incremental shortening is much less (0.01 Å) as complexes become more sulfur-rich; Mo and W complexes are intermediate. These data suggest that metal $d\pi$ –ligand $p\pi$ bonding weakens in the order $\text{V} > \text{Mo}, \text{W} > \text{Re}$. As the ligands sets are identical it seems reasonable to infer that the changes reflect intrinsic metal π -bonding power.

Discussion

In this paper we report a structural analysis of transition-metal chalcogenido complexes in a variety of geometries and oxidation states. Agreement is very good in the large majority of cases between structures calculated with effective core potential methods and structures determined by X-ray, electron diffraction, and microwave data. The good agreement for heavier chalcogens is of particular interest since it is well accepted that TM $d\pi$ –MG $p\pi$ bonding becomes weaker for heavier MG congeners,² a circumstance which can exacerbate the electron correlation problem.¹⁰⁰ In a previous study of $\text{TM}=\text{Si}$ complexes, electron correlation was found to be of importance in obtaining even a qualitative description of the $\text{TM}=\text{Si}$ double bond.^{15j} Phosphinidene ($\text{L}_n\text{M}=\text{PR}$) complexes are intermediate between silylenes and sulfidos making their study of great interest.^{15k} The present paper provides convincing evidence that computational methods employed are adequately describing the electronic structure of these diverse TM–chalcogenido complexes.

Based on orbital overlap arguments²⁻⁴ the $\text{TM}=\text{Ch}$ bond in the WCl_4Ch and TaCl_3Ch can be considered a triple bond (two orthogonal $d\pi$ orbitals on the metal can overlap two orthogonal $p\pi$ orbitals on Ch). For metalates there are eight Ch $p\pi$ orbitals, clearly too many for all four Ch to form a double bond so that the WCh bond order must be less than 2, as comparison of WCh bond lengths for $d^0\text{-WCl}_4\text{Ch}$ and $d^0\text{-WCh}_4^{2-}$ makes clear. Despite the increased coordination number of WCl_4Ch (ionic radii of W^{6+} are 0.56 and 0.65 Å for coordination numbers 4 and 5, respectively¹⁰¹), WCh bond length in WCl_4Ch are shorter by ≈ 0.15 Å. Additionally, metric and vibrational data for $[\text{M}(\text{O})_x(\text{S})_{4-x}]^{q-}$, Table 9, highlights the competition for $\text{TM } d\pi\text{--Ch } p\pi$ bonding in mixed thiometalates: $\text{TM}=\text{oxo}$ and $\text{TM}=\text{sulfido}$ bond lengths increase as the complex becomes more oxygen-rich. Interestingly, WCh bond lengths in WCl_2Ch_2 , Table 6, are ≈ 0.03 Å longer than those in WCl_4Ch , Table 4, an observation counter to the lengthening one typically observes for analogous bond types upon increasing coordination number; the fundamental description

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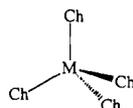
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Table 8.

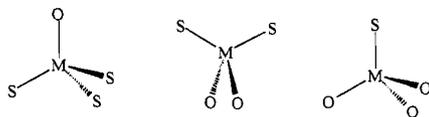
[M(O) ₄] ^{q-} Complexes ^a											
	V	Nb	Ta	Cr	Mo	W	Mn	Tc	Re	Ru	Os
M-O _{calc}	1.72	1.87	1.87	1.61	1.76	1.77	1.55	1.69	1.70	1.66	1.66
M-O _{expt}	1.71	1.89	NA	1.65	1.77	1.78	1.61	1.71	1.72	1.71	1.70
ν _{MO}	792	732	733	949	894	899	988	1011	1024	899	1093
k _{MO}	4.50	4.30	4.66	6.50	6.47	7.01	7.12	8.27	9.11	7.01	10.94
[M(S) ₄] ^{q-} Complexes											
	V	Nb	Ta	Cr	Mo	W	Mn	Tc	Re		
M-S _{calc}	2.19	2.33	2.33	2.07	2.20	2.21	2.03	2.12	2.13		
M-S _{expt}	2.16	2.27	2.28	NA	2.17	2.17	NA	NA	NA		
ν _{MS}	423	396	378	441	468	451	326	511	502		
k _{MS}	2.07	2.20	2.29	2.30	3.12	3.26	1.27	3.07	4.05		
[M(Se) ₄] ^{q-} and [M(Te) ₄] ^{q-} Complexes											
	V/Se	Nb/Se	Ta/Se	Mo/Se	W/Se	W/Te					
M-Ch _{calc}	2.32	2.46	2.46	2.33	2.34	2.57					
M-Ch _{expt}	NA	2.387(6)–2.403(1)	2.369(1)–2.397(6)	2.293(1)	2.314(1)	NA					
ν _{MCh}	292	267	239	311	285	206					
k _{MCh}	1.56	1.80	1.86	2.50	2.66	1.90					

^a All complexes are T_d minima. Experimental data are from refs 2–5, 98, and 99.

Table 9. Calculated [M(O)_x(S)_{4-x}]^{q-} Geometries^a

	V	Mo	W	Re
		x = 1		
MO	1.58 Å	1.69 Å	1.70 Å	1.67 Å
MS	2.25 Å	2.24 Å	2.25 Å	2.14 Å
ν _{MO}	1054	1012	1022	1067
k _{MO}	7.97	8.30	9.06	9.88
ν _{MS}	388	449	433	492
k _{MS}	1.74	2.86	3.00	3.88
		x = 2		
MO	1.62 Å	1.71 Å	1.72 Å	1.68 Å
MS	2.34 Å	2.28 Å	2.29 Å	2.17 Å
ν _{MO}	999	988	998	1063
k _{MO}	7.15	7.90	8.62	9.82
ν _{MS}	340	427	412	483
k _{MS}	1.33	2.59	2.72	3.75
		x = 3		
MO	1.66 Å	1.73 Å	1.74 Å	1.69 Å
MS	2.46 Å	2.33 Å	2.34 Å	2.20 Å
ν _{MO}	905	942	948	1041
k _{MO}	5.87	7.19	7.79	9.40
ν _{MS}	272	400	387	469
k _{MS}	0.86	2.27	2.40	3.54

^a For x = 2 the minima are C_{2v}; for x = 1, 3 the minima are C_{3v}.



of the WCh bond lengths must therefore be different in WCl₂Ch₂ and WCl₄Ch. For this reason and given the observation of small competition between Ch and Ch' in WCl₂(Ch)(Ch'), see Table 6, we favor a description of WCh bonds in WCl₂Ch₂ which is weighted toward a double bond. A maximum of three TM dπ–Ch pπ bonds are possible for a tetrahedral complex, so that E is not possible, while F–H are expected to dominate. Structures F and G would make

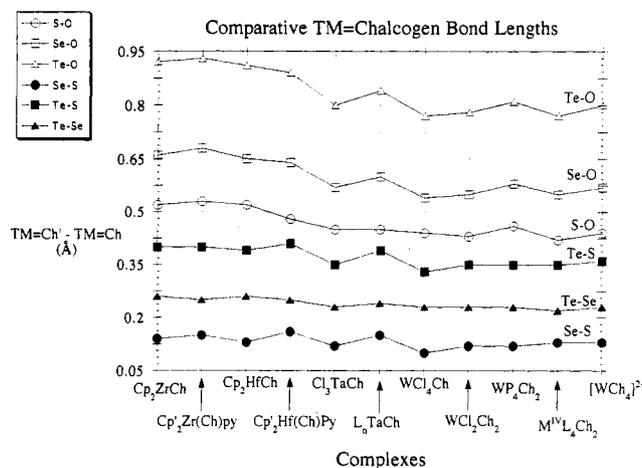
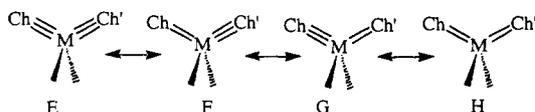


Figure 1. Comparative TM–chalcogen bond lengths ($R_{MCh'}-R_{MCh}$) from experimental (Cp₂Zr(Ch)py, Cp₂Hf(Ch)py, L₃TaCh, and M^{IV}L₄Ch₂) and calculated (remaining entries) data; see footnotes in Table 10.

equivalent contributions for Ch = Ch'; if F and G were major contributors, replacement of Ch' with a stronger π-bonding ligand (e.g., WCl₂Se₂ → WCl₂SeO) should lead to F making a much larger contribution and a significantly shorter WCh' bond length (and larger WCh' force constant) which the calculations indicate does not happen, see Table 6. A description such as H is consistent with the notion that the chalcogenido ligands in WCl₂(Ch)(Ch') (and presumably other d⁰ *cis*-di(chalcogenido) complexes) exist in relative electronic isolation.

Recent experiments provide an opportunity to probe TM=MG multiple bonding bond as a function of position in the Periodic Table. For complexes where there is data for an entire series of nonradioactive chalcogens we have plotted relative bond lengths ($R_{MCh'}-R_{MCh}$) for experimental and computational models in Figure 1; the data are collected in Table 10. Inspection of Figure 1 and Table 10 shows that other than the Zr- and Hf-oxos (experimental and computational models) there is similar behavior in relative bond lengths despite widely varying chemical environments. Relative bond lengths versus oxo (S–O, Se–O, and Te–O in Table 10) in group IVB systems tend to be larger than for other families of complexes. Relative bond lengths for heavier

Table 10. Relative Bond Lengths for Transition-Metal Systems

complex	S-O ^a	Se-O	Te-O	Se-S	Te-S	Te-Se
*Cp ₂ ZrCh	0.52	0.66	0.92	0.14	0.40	0.26
Cp' ₂ ZrCh(py)	0.53	0.68	0.93	0.15	0.40	0.25
*Cp ₂ HfCh	0.52	0.65	0.91	0.13	0.39	0.26
Cp' ₂ HfCh(py)	0.48	0.64	0.89	0.16	0.41	0.25
*TaCl ₃ Ch	0.45	0.57	0.80	0.12	0.35	0.23
L _n TaCh ^b	0.45	0.60	0.84	0.15	0.39	0.24
*WCl ₄ E ^c	0.44	0.54	0.77	0.10	0.33	0.23
*WCl ₂ Ch ₂	0.43	0.55	0.78	0.12	0.35	0.23
*W(PH ₃) ₄ (Ch) ₂	0.46	0.58	0.81	0.12	0.35	0.23
M ^{IV} L ₄ Ch ₂ ^d	0.42	0.55	0.77	0.13	0.35	0.22
*[WE ₄] ²⁻	0.44	0.57	0.80	0.13	0.36	0.23

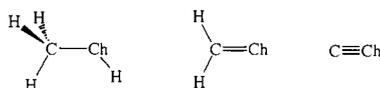
^a Difference in bond lengths for ECP calculated (*) and experimental TM-chalcogenido complexes. ^b Experimental L_nTaCh values were obtained from the following Ta^V complexes: Ch = O (TaO(N-iPr)₂)₃; ²Ch = S (average of eight reported Ta^V = S complexes),⁴¹⁻⁴³ Ch = Se and Te (2-Se and 2-Te).^{44a} ^c These are the calculated WCh bond lengths; experimental data for WCl₄Ch¹⁴ show similar relative bond lengths for characterized examples (Ch = O, S, and Se). Similar agreement is found for the three experimentally characterized members of the [W(Ch)₄]²⁻ family. ^d Data for these systems come from d², group VIB, *trans*-bis(chalcogenido) complexes: Ch = O ([Mo(O)₂(CN)₄]⁴⁻),⁸⁵ Ch = S (W(PMe₃)₂(CN-t-Bu)₂(S)₂);⁷⁷ Ch = Se (W(PMe₃)₄(Se)₂);⁷⁸ Ch = Te (W(PMe₃)₄(Te)₂).¹¹

Table 11. Relative Bond Lengths for Organic Systems

	C-Ch ^a	C=Ch ^b	C≡Ch ^c
O	1.41 Å	1.20 Å	1.13 Å
S	1.82 Å	1.61 Å	1.53 Å
Se	1.96 Å	1.74 Å	1.66 Å
Te	2.16 Å	1.95 Å	1.88 Å

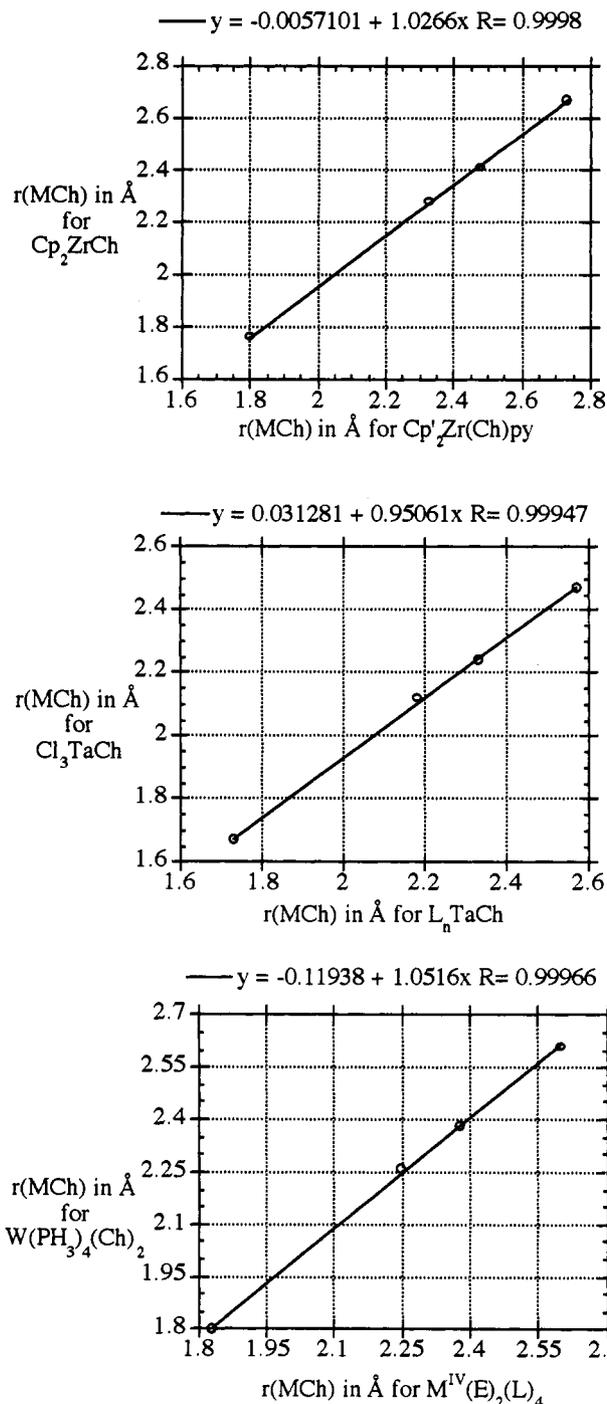
	S-O ^d	Se-O	Te-O	Se-S	Te-S	Te-Se
M-Ch	0.41 Å	0.55 Å	0.75 Å	0.14 Å	0.34 Å	0.20 Å
M=Ch	0.41 Å	0.54 Å	0.75 Å	0.13 Å	0.34 Å	0.21 Å
M≡Ch	0.40 Å	0.53 Å	0.75 Å	0.13 Å	0.35 Å	0.22 Å

^a ECP calculated C-chalcogen bond length in methanol (C₁) and heavier derivatives. ^b ECP calculated C-chalcogen bond length in formaldehyde (C_{2v}) and heavier derivatives. ^c ECP calculated C-chalcogen bond length in carbon monoxide (C_{∞v}) and heavier derivatives. ^d Difference in ECP calculated bond lengths for different bond types; Ch-Ch' = R_{CCh} - R_{CCh'}.



chalcogens (Se-S, Te-S, and Te-Se) show less variation regardless of TM complex. As a further probe, ECP calculations were carried out (using the same approach outlined in Computational Methods) on organic compounds with prototypical single (H₃C-Ch-H), double (H₂C=Ch), and triple (C≡Ch) bonds. Relative bond lengths for organic systems, Table 11, show similar behavior to non-metallocene complexes in Table 10. Parkin et al.¹³ have discussed similar considerations based on ZrCh bond length data for CpZr(Ch)(py) and our preliminary ECP calculations. Analysis of ECP wave functions for Cp₂ZrCh in which delocalized RHF molecular orbitals have been transformed into localized variants¹⁰² clearly points to a greater contribution from a singly-bonded Zr-Ch structure (relative to Zr=Ch) when Ch is O compared to sulfido, selenido, and tellurido analogues. The ZrO π-bonds are significantly more localized on the oxo ligand. Taken together, the data suggest that in WCl₄Ch, [W(Ch)₄]²⁻, WL₄(Ch)₂, and TaCl₃Ch the nature of the TMCh bond is similar for all chalcogens, while there is a fundamental difference in the Zr-oxo (and Hf-oxo) bond in relation to heavier chalcogens.

In previous studies of TM=MG complexes¹⁵ we have focused on the ability of ECPs to make computations feasible for complexes incorporating transition metals from the lightest to heaviest members of a triad. Transition metals studied here include the entire portion of the transition series for which multiply-bonded chalcogenides have been structurally characterized, i.e., Ti-through Co-triads. The present work also evaluates ECP methods

**Figure 2.** Plots of calculated versus experimental TM-Ch bond lengths for models in which the entire series of nonradioactive chalcogens have been experimentally determined.

as a tool for addressing the chemistry of heavier MG elements. All nonradioactive chalcogens (i.e., O, S, Se, Te) are included in the ECP study. With few exceptions, agreement between theory and experiment is excellent. In Figure 2 calculated versus experimental bond lengths are plotted for complexes in which there is an entire series of chalcogenidos (Ch = O, S, Se, Te): Cp₂ZrCh vs Cp'₂Zr(Ch)(py) (Cp₂HfCh vs Cp'₂Hf(Ch)(py) shows equally good agreement), Cl₃TaCh vs L_nTaCh, and *trans*-W(PH₃)₄(Ch)₂. Inspection of linear least-squares fit lines in Figure 2 shows the slopes and correlation coefficients to be near unity, while intercepts are close to zero. Additionally, complexes for which three members (Ch = O, S, Se) have been experimentally characterized, e.g., WCl₄Ch¹⁴ and [M(Ch)₄]²⁻,^{2,5,98,99} also show good agreement with calculated data for heavy and light chalcogens (*vide supra*). The satisfactory results and growing

importance of heavier MG elements in electronics and materials applications suggests that the study of TM complexes involving the heavier chalcogens with effective core potentials will be a fruitful area of computational research in the future.

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