Further studies of the transfer reaction and additional complexation chemistry would appear to be worthwhile.

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Registry No. **9**, 139732-78-8; **12**, 139732-79-9; **13**, 139732-80-2; **14**, 139732-81-3; **15**, 139732-82-4; **16**, 139732-83-5; **17a**, 139732-89-1; **17b**, 139732-90-4; **20**, 139732-86-8; **22**, 139732-84-6; **23**, 139732-85-7; **24**, 139732-87-9; **25**, 139732-88-0; $(CF_3P)_4$, 393-02-2; $(CF_3P)_5$, 745-23-3; $Pt(\eta^2\text{-}C_2H_4)(PPh_3)_2$, 12120-15-9; $Pt(PEt_3)_3$, 39045-37-9; $Pt(PEt_3)_4$, 33937-26-7; $Pt(PMe_2Ph)_4$, 33361-89-6; $Pt(PPh_3)_4$, 14221-02-4; $Pd(PPh_3)_4$, 14221-01-3; $Ni(dppe)_2$, 15628-25-8; $Pd(dppe)_2$, 31277-98-2.

Supplementary Material Available: Listings of crystallographic data, positional parameters, and anisotropic and equivalent isotropic thermal parameters (Tables S1–S3), root-mean-square amplitudes of thermal vibrations (Table S4), all interatomic distances (Table S5) and angles (Table S6), torsional angles (Table S7), and weighted least-squares planes (Table S8) (13 pages); a table of calculated and observed structure factors (Table S9) (41 pages). Ordering information is given on any current masthead page.

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Synthesis, Structure, and Bonding Properties of a New Volatile [*N*-*tert*-Butyl(1*H*-pyrrol-2-ylmethylene)aminato]thallium(I) Complex

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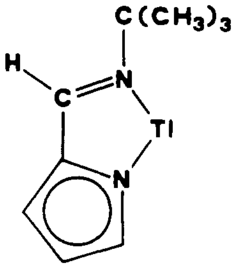
The synthesis, characterization, structure, and bonding properties of the title complex are reported. The complex consists of monomeric units in the vapor phase. Geometrical structural parameters have been fully optimized using relativistic pseudopotential extended basis set gradient ab initio calculations. The most stable conformation was found to have a planar geometry with slightly different Tl–N bond distances. The metal–ligand bonding is σ-only in nature and involves strong mixing between several ligand-based valence molecular orbitals and both filled 5s and virtual 5p thallium atomic orbitals. The photoelectron spectra of the complex are in consistent agreement with this bonding description and further underscore the covalent nature of the metal–ligand bonding.

Introduction

The synthesis and structural characterizations of low-coordinated thallium(I) complexes has recently attracted considerable attention.[1] In addition, thallium(I) complexes act as mild transfer reagents for organic and inorganic ligands, yielding products unobtainable by conventional methods,[2] while volatile thallium compounds are better suited precursors for the MOCVD growth of thin films of superconducting Tl–Ba–Ca–Cu–O phases.[3] The metal–ligand bonding in thallium(I) complexes remains, however, still open to question, since only a few studies have been reported[4,5] and, in addition, relativistic effects due to the heavy metal certainly play a significant role.[4]

In this paper we report the synthesis, characterization, and electronic structure of a new thallium(I) volatile complex: [*N*-*tert*-butyl(1*H*-pyrrol-2-ylmethylene)aminato]thallium(I) (hereafter Tl(L), I).

The study combines experimental measurements using variable (He I and He II) photon source vapor-phase photoelectron (PE) spectroscopy and relativistic pseudopotential ab initio calculations to perform the geometry optimization, to study the ground-state electronic properties, and, together with ΔSCF calculations, to evaluate ionization energies (IEs).



I

Experimental Section

Synthesis of Tl(L). The synthetic procedures were always conducted in strictly anhydrous solvents and under a prepurified N_2 atmosphere using the Schlenk method. Pyrrole-2-carboxaldehyde (9.5 g) (Aldrich Chemical Co.) and *tert*-butylamine (10.5 mL) (Fluka) were condensed into absolute ethanol (50 mL). The solution was allowed to stand for several hours at room temperature. Thallous ethoxide (1:1 molar ratio) (Fluka) was added dropwise. The white precipitate was filtered off and purified (yield 21%) by sublimation at 160 °C in vacuo (10^{-3} Torr); mp 260 °C dec. The compound appears almost insoluble in most common solvents. It slightly dissolves in DMSO even though any attempt to grow crystals by slow diffusion methodologies was unsuccessful. EI MS (18 eV), *m*/*z* (relative intensity): 354, 352 (M^+, 79, 39), 339, 337 ($(M - Me)^+$, 26, 11), 205, 203 (^{205}Tl, ^{203}Tl, 100, 62), 150 (HL^+, 18), 135 ($(HL - Me)^+$, 25). IR (Nujol mull): $\nu(C{=}N)$ 1608 cm^{-1}. ^1H NMR (DMSO-d_6, 250 MHz, TMS external reference): δ 1.28 (s, 9 H, CMe_3), 6.04 (q, 1 H, pyr), 6.54 (q, 1 H, pyr), 6.83 (d, 1 H, pyr), 8.65 (s, 1 H, CH). Anal. Found (calcd): Tl, 58.1 (57.8); C, 30.2 (30.6); N, 8.5 (7.9); H, 3.6 (3.7).

Physical Measurements. ^1H NMR spectra were obtained on a Bruker AC-250 spectrometer. IR spectra were recorded on a Perkin-Elmer 684 infrared spectrophotometer. The melting point was determined on a Mettler TA4000 microcalorimeter. Elemental microanalyses were performed in the Analytical Laboratories of the University of Catania. EI and FAB mass spectra (MS) were recorded on a Kratos MS 50 dou-

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Table I. Negative-Ion FAB Mass Spectrum of Tl(L)

m/z	rel abund[a]	assgnt	m/z	rel abund[a]	assgnt
150	100	$[HL]^-$	1110	... (0.01)	$[Tl_4(L)_2]^-$
352	16 (14)	$[Tl(L)]^-$	1112	... (0.1)	
354	34 (34)		1114	0.6 (0.4)	
555	1.3 (1.0)	$[Tl_2(L)]^-$	1116	0.7 (0.7)	
557	3.6 (4.7)		1118	0.6 (0.3)	
559	5.6 (5.6)		1259	... (0.02)	$[Tl_4(L)_3]^-$
704	1.8 (1.4)	$[Tl_2(L)_2]^-$	1261	... (0.2)	
706	7.6 (6.7)		1263	0.7 (0.6)	
708	8.0 (8.0)		1265	1.0 (1.0)	
907	0.4 (0.1)	$[TL_3(L)_2]^-$	1267	0.6 (0.6)	
909	1.2 (1.1)		1408	... (0.007)	$[Tl_4(L)_4]^-$
911	2.6 (2.6)		1410	... (0.07)	
913	2.2 (2.1)		1412	0.3 (0.2)	
1056	... (0.1)	$[Tl_3(L)_3]^-$	1414	0.3 (0.3)	
1058	0.8 (0.7)		1416	0.2 (0.2)	
1060	1.8 (1.8)				
1062	1.4 (1.4)				

[a] Predicted values in parentheses.

ble-focusing mass spectrometer equipped with a standard FAB source. Negative-ion FAB MS spectra were obtained using diethanolamine and tetramethylurea (1:1) as the matrix. Mass resolution was approximately 2000. Oligomeric structures up to tetramers were found (Table I). Their FAB MS patterns accurately fit the expected statistical distribution of natural isotopes. PE spectra were recorded with the aid of a photoelectron spectrometer interfaced to an IBM PC AT computer as described elsewhere.[6] Procedures used to "lock" the energy scale to defined internal references have also been described previously.[6] Spectral resolution measured on the Ar^+ $^2P_{3/2}$ peak was always better than 0.030 eV.

Computational Details

Ab initio effective core potential (ECP) gradient calculations were used for geometry optimization. Relativistic ECPs and bases of Wadt and Hay[7] were used for Tl. Stevens'[8] and Dunning's[9] ECPs and bases were adopted for C, N, and H atoms, respectively. Thallium 5d electrons were included either in the core, in the 3-electron ECP calculations, or were treated as valence electrons in 13-electron ECPs.[7] Effects due to basis sets were tested with 3-electron ECPs using double-ζ (DZ-3) and triple-ζ (TZ-3) Gaussian basis sets, as well as including d-polarization functions for the Tl atom ($\zeta = 0.146$)[10] (TZd-3). The triple-ζ basis set (TZ-13) was used for 13-electron ECP calculations.

The model *N*-methyl complex (Tl(L′)) was adopted for geometry optimization. Optimizations were always said to converge when the maximum gradient was less than 5×10^{-4} hartree/au. A planar arrangement of the model complex (C_s symmetry) was assumed as starting geometry. The HONDO-8 code[11] was used.

Ionization energies were evaluated using ΔSCF pseudopotential restricted Hartree–Fock ab initio calculations[6] on the Tl(L) complex in the optimized geometry using the PSHONDO program.[12] Pseudopotentials and basis sets of DZ quality were used.[13]

The HONDO and PSHONDO codes were implemented on an IBM 9370 minicomputer.

Results and Discussion

Bonding of the Tl(I) atom involves the formation of a five-membered chelate ring (I). Thus, the pyrrole NH stretching ($\sim$3460 cm^{-1})[14] is absent in the IR spectrum, while the C=N stretching frequency shifts to lower values (1608 cm^{-1}), as always found in closely related systems.[15] In accordance with the increased anionic character of the ligand upon complexation, ring proton ^{1}H NMR signals slightly shift toward higher field relative to corresponding resonances of the free ligand.[16] Moreover, the ^{1}H NMR imine resonance shifts to lower field, as found in other main group heavy metal homologous complexes.[14] FAB MS spectral patterns (Table I) could be indicative of an oligomeric aggregation in the liquid matrix, since clusters up to tetramers are found.[17] Reorganization processes after ionization cannot be, however, ruled out. By contrast, EI MS spectra have patterns which do not depend upon the energy (10–70 eV) of bombarding electrons with an m/z 354 molecular ion peak and, therefore, are clearly indicative of a monomeric structure of the complex in the vapor phase.

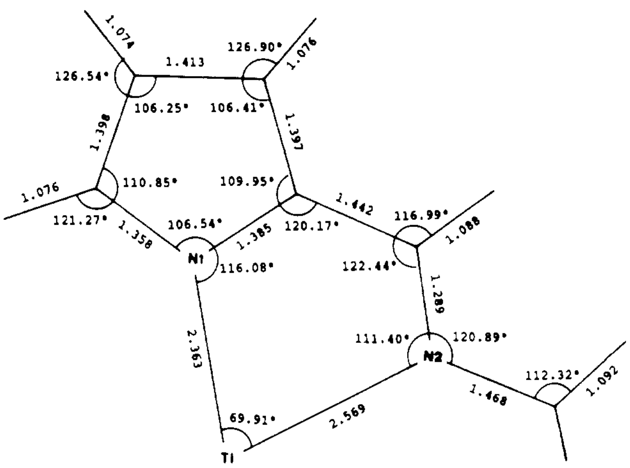

Figure 1. Optimized geometry of the model Tl(L′).

Table II. Selected Optimized Geometrical Parameters (Å; deg) for the Model Tl(L′)

	DZ-3	TZ-3	TZd-3	TZ-13
Tl–N1	2.264	2.256	2.253	2.363
Tl–N2	2.494	2.487	2.479	2.569
N1–Tl–N2	71.96	71.82	69.17	69.91

Fully optimized structural parameters of the model Tl(L′) are reported in Figure 1. The structure consists of a planar geometry whose geometrical data agree well with those of the simpler HL′ ligand reported in a previous paper.[18] No remarkable changes are due to the coordinated metal center. The Tl–N1 distance is appreciably shorter (0.2 Å) than found with the Tl–N2 bond length. The average Tl–N distance (2.466 Å) appears however clearly shorter than in other N-coordinated Tl(I) complexes.[19] Nevertheless, present geometrical data represent the first case of a Tl(I) complex with lower (than 3) coordination number. The average distance, however, compares well with the 2.58 Å length found in three-coordinated Tl(HB(pz)$_3$)[19a] (HB(pz)$_3$ = hydrotris(1-pyrazolyl)borate anion). Finally, it is worthy of note that

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Table III. Eigenvalues and Population Analysis of the Outermost Tl(L) MOs

		% pop.[a]							overlap pop.[a]		
		Tl									
MO	eigenvalue, −eV	6s	6p	N2	N1	CH_{im}	CH_{pyr}	CMe_3	Tl–N2	Tl–N1	dominant character
9a″	7.34			15			83	2	0.000	0.000	π_4
8a″	8.59		1		35		64		0.000	0.032	π_3
22a′	8.71	55	16	9	12		4	4	−0.198	−0.262	Tl 6s
21a′	11.29	1	5	35	20	7	11	21	0.110	0.020	n_{im}, n_{pyr}
7a″	11.49			25	4	24	13	34	0.000	0.000	π_2
6a″	12.98			10	2	2	4	82	0.000	0.000	$\pi(CMe_3)$
20a′	13.10	2		3	4	2	5	84	−0.012	0.024	$\sigma(CMe_3)$
19a′	13.52	16		7	9	3	50	15	0.050	0.118	σ, Tl 6s
5a″	13.65					1	1	98	0.000	0.000	$\pi(CMe_3)$
18a′	14.35	1		4	6	3	69	17	0.016	0.012	σ
17a′	14.51	10		3	14		59	14	0.030	0.078	σ, Tl 6s

overall charge		overlap pop.[a]	
Tl = $6s^{1.871}$, $4p^{0.529}$ = +0.600 pyrrole ring = −0.577	–CH=N– = −0.226 $-CMe_3$ = +0.203	Tl–N1 = 0.160	Tl–N2 = 0.106

[a] See Figure 1; im and pyr subscripts refer to the imine and pyrrole atoms, respectively.

Table IV. Experimental IEs, Computed IEs, and Assignments of the PE Spectrum of Tl(L)

band label	IE, eV			assgnt[b]
	exptl	ΔSCF	PT[a]	
a	7.29	6.37	6.85	9a″
b	8.18	7.29	7.71	8a″
c	8.73	7.98	8.40	22a′
d	9.55	9.99	9.97	21a′
e	10.10	10.45	10.57	7a″
x	19.57			"$^2D_{5/2}$"
x′	21.79			"$^2D_{3/2}$"

[a] Perturbative values take into account repolarization contributions scaled by a factor of 0.75 (see ref 6). [b] See Table III.

the present average value is clearly close to the sum of covalent radii (2.23 Å) of atoms involved in the bonding, thus indicating its predominantly covalent nature.

Table II reports selected geometrical parameters obtained with different basis sets (DZ and TZ), as well as by including either 5d atomic orbitals (AOs) in the valence set or 6d polarization functions. Differences among Tl–N distances due to different basis sets are almost negligible (0.3%). Moreover, in accordance with previous results on Tl(η^5-C_5H_5),[4d] inclusion of 6d polarization functions does not significantly affect geometrical results. By contrast, inclusion of 5d AOs causes an appreciable increase of the Tl–N distances (~0.1 Å, 4.2%), thus indicating that the 5d $\langle r^2 \rangle$ expectation value represents a relevant factor as far as the Tl–N equilibrium distance is concerned.[7,20]

Bonding in Tl(L). Table III collects ground-state results for Tl(L). Remarkable metal admixtures are only found in a few molecular orbitals (MOs). The remainder are almost unperturbed counterparts of analogous MOs of the free ligand;[18] in particular π_3 and π_4 represent the lower lying π MOs on the pyrrole ring, while π_2 possesses a dominant π C=N character.

Metal–ligand bonding appears σ-only in nature. It involves a two-orbital two-electron stabilizing interaction which causes donation of electron densities from both the N_{2p} imine and pyrrole lone pairs (n_{im} and n_{py}) into the empty Tl 5p orbital and is represented by the 21a′ MO (Table III). Accordingly, this MO provides a positive contribution to the Tl–N overlap population. The Tl $6s^2$ "inert" lone pair, responsible for the formal $6s^2$ configurations of Tl(I) complexes, is clearly represented by the 22a′ MO, and it is strongly admixed into various MOs because of four-electron interactions involving σ systems mainly localized on the pyrrole ring and responsible for the prototropic properties of the ligand itself. These interactions cause the destabilization of the 6s-based MO (22a′) whose antibonding character appears considerably reduced because of a competing bonding admixture with the Tl $6p_y$ (16%) AO. The total Tl–N overlap population is positive, even though singling-out of individual contributions due to various MOs shows that the Tl–N bonding results from the balancing of, sometimes opposite, contributions due to 6s and 6p AOs.

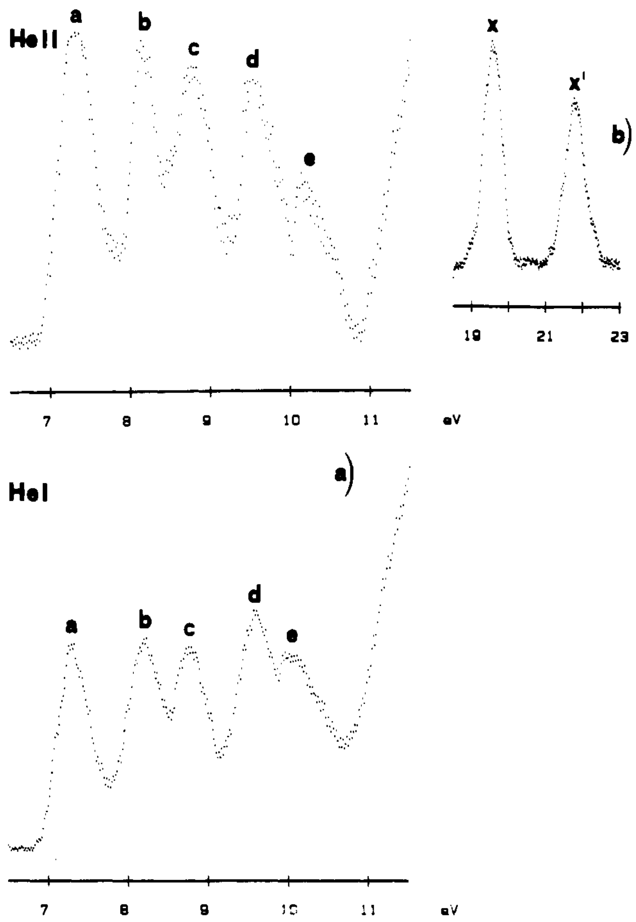

Figure 2. (a) He I and He II PE spectra of Tl(L) in the low-IE region. (b) He II spectrum in the higher IE region.

The PE spectrum of Tl(L), consists in the low-IE region (<10.5 eV) of five well-resolved bands (a-e) (Figure 2) having almost comparable relative intensities in both He I and He II spectra. The higher energy region has a general appearance resembling those found in closely related molecules[18] and represents ionizations of MOs of no relevance in the M–L bonding. Two further bands, forming an intense doublet (x, x′), are apparent in the He II

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spectrum (Figure 2) in the 19–23-eV IE region.

ΔSCF ab initio IE values (Table IV) provide an accurate fitting of experimental IE values. Thus, bands a and b represent the ionization of 9a″ (π_4) and 8a″ (π_3) MOs, while bands c–e represent the ionization of 22a′, 21a′, and 7a″ MOs, respectively.

This assignment is consistent with previous PE data for closely related species, including several Tl(I) complexes.[21] It is noted, however that the IE presently attributed to 22a′ MO represents the lowest value reported to date[21,22] for 6s^{-1} ionization in Tl(I) compounds (Table IV). Besides the effects due to the partial charge on the Tl atom and with the assumption of no differential relaxation energies upon ionization among the various Tl(I) complexes, this observation points to a more extensive covalent 6s–a′ mixing.

Finally, we discuss the higher IE doublet (x, x′ in Figure 2) structure. Reference to literature data clearly indicates that the features must be related to the $^2D_{5/2}$ and $^2D_{3/2}$ multiplet states produced upon production of the ionized 5d^9 configuration of the metal center.[21,22a] As already observed for other "covalent" Tl(I) complexes,[21] there is no evidence of any fine structure due to "ligand field" splitting, which, conversely, proved ubiquitous in the spectra of Tl(I) halides.[22a] This observation points to a "corelike" behavior of 5d subshells mostly sensitive to electrostatic perturbations rather than to covalent mixing involving differential overlaps. Finally, the average metal 5d IE (20.45 eV) is close to the lowest value observed to date for Tl(HB(pz)$_3$)[21b] and consistently lower than the value observed for the Tl atom.[22a] This "chemical shift" has, however, been interpreted in terms of "extraatomic" relaxation due to the more polarizable ligand framework.[21c]

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Registry No. I, 139377-73-4; pyrrole-2-carboxaldehyde, 1003-29-8; *tert*-butylamine, 75-64-9.

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Faculty of Science, Tohoku University, Aramaki, Aoba-ku Sendai 980, Japan

Synthesis, Structure, and Properties of Oxidized Hexamolybdenum Clusters $[(Mo_6X_7Y)X'_6]^{2-}$ (X = X′ = Cl, Br; Y = S, Se)

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The synthesis, structure, and properties of Mo_6(13+) species, which are obtained by the oxidation of Mo_6(12+) species $[(Mo_6X_7Y)X'_6]^{3-}$ (X = X′ = Cl, Br; Y = S, Se), are reported. $(n\text{-}Bu_4N)_2[(Mo_6Cl_7S)Cl_6]$ crystallizes in the monoclinic space group $P2_1/n$ with a = 18.542 (2) Å, b = 11.701 (2) Å, c = 12.806 (2) Å, β = 90.21 (1)°, V = 2778.5 (7) Å^3, and Z = 2. $(n\text{-}Bu_4N)_2[(Mo_6Cl_7Se)Cl_6]$ crystallizes in the monoclinic space group $P2_1/n$ with a = 18.571 (2) Å, b = 11.685 (1) Å, c = 12.845 (1) Å, β = 90.12 (1)°, V = 2787.1 (5) Å^3, and Z = 2. $(n\text{-}Bu_4N)_2[(Mo_6Br_7S)Cl_6]$ also crystallizes in the monoclinic space group $P2_1/n$ with a = 18.740 (2) Å, b = 11.647 (2) Å, c = 13.030 (2) Å, β = 90.05 (1)°, V = 2844.0 (7) Å^3, and Z = 2. The Mo_6(12+) species $(Et_4N)_3[(Mo_6Br_7S)Cl_6]$ crystallizes in the tetragonal space group $P4_2/mnm$ with a = 11.968 (1) Å, c = 16.804 (2) Å, V = 2406.8 (4) Å^3, and Z = 2. The Mo–Mo distances of the Mo_6(13+) clusters (2.626 (3) Å in $[(Mo_6Cl_7S)Cl_6]^{2-}$, 2.628 (3) Å in $[(Mo_6Cl_7Se)Cl_6]^{2-}$, 2.653 (3) Å in $[(Mo_6Br_7S)Cl_6]^{2-}$) are slightly longer than those of the corresponding Mo_6(12+) species. Absorption peak positions in the 1800-nm (5320–6060 cm^{-1}) and 900-nm regions (10 500–11 200 cm^{-1}) are independent of the capping and terminal ligands, but those in the range 480–650 nm (15 400–20 400 cm^{-1}) depend on the ligand. Their ESR spectra at 77 K are axially symmetric ($g_\perp$ = 2.12–2.15, $g_\parallel$ = 2.05–2.07). The electronic structure is discussed on the basis of these data.

Hexamolybdenum clusters provide various complexes with halides or chalcogenides as capping or terminal ligands. The complexes with eight capping halides $[(Mo_6X_8)X'_6]^{2-}$ (X = X′ = Cl, Br, I; Mo_6,12+), are discrete ions, give strong red emissions,[2,3] and are oxidized and reduced with difficulty.[2] On the other hand, those with eight capping chalcogenides, $Mo_6Y_8^{n-}$ (Y = S, Se, Te), are nonstoichiometric in the superconducting solid Chevrel phase, in which the total oxidation number of six molybdenum atoms is in the range 12+ to 16+.[4] (For convenience the oxidation number of Mo_6 moiety is expressed in parentheses after the moiety.) Although a variety of discrete hexamolybdenum clusters of Mo_6(12+) were reported,[5-7] halide clusters with oxidized

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