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Electronic Structure of Bimetallic "Flyover-Bridge" Derivatives. UV-PES and ab Initio Study of $Fe_2(CO)_6[(R-C_2-R)_2CO]$ and $Ru_2(CO)_6[(R-C_2-R)_2CO]$ ($R = C_2H_5$)

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The gas-phase UV-photoelectron (UV-PE) spectra of hexacarbonyl[μ-(1,2,5-η:1,4,5-η)-3-oxo-1,2,4,5-tetraethyl-1,4-pentadiene-1,5-diyl]diiron(*Fe-Fe*) (**1**) and -diruthenium(*Ru-Ru*) (**2**) ("flyover-bridge" complexes) are reported. The assignment of experimental data has been carried out by means of theoretical results obtained by the ab initio pseudopotential method. The main source of bonding between $M_2(CO)_6$ and the organic fragment has been found to imply an interaction between metal and the terminal carbon atoms of the organic moiety essentially σ in nature.

Introduction

It is well-known that the reaction between alkynes and iron carbonyls [$Fe(CO)_5$, $Fe_2(CO)_9$, and $Fe_3(CO)_{12}$] affords a plethora of stable organometallic complexes, with nuclearity ranging from one to four iron atoms with several organic products.[2] Generally, alkyne oligomerization takes place (with or without CO insertion) giving rise to different and quite unusual coordination modes of the organic moiety over the metal atom(s). Among oligomerization compounds, the authors have already studied the electronic structure of "ferrole" complexes, namely $Fe_2(CO)_6(RC_2R)_2$ and $Fe_3(CO)_8(RC_2R)_2$.[3a]

Another interesting class of organometallic products, obtained in high yield from the aforesaid reaction, has general formula $Fe_2(CO)_6[(R-C_2-R)_2X]$ where $X = CH_2$ or CO. The crystal structures obtained by Piret et al. ($R = H$, $X = CH_2$),[4a] by Piron et al. ($R = Me$, $X = CO$),[4b] and by Cotton et al. ($R = Ph$, $X = CO$)[4c] pointed out an unusual arrangement, where the two iron atoms are symmetrically bridged by the twisted fulvene[4a] or by the twisted dienone chain[4b,c] (see Figure 1). The equivalent environment of the two $Fe(CO)_3$ units has been confirmed by Mössbauer[5] as well as VT ^{13}C NMR spectroscopies.[4c,6]

Interestingly, $Fe_2(CO)_6[(R-C_2-R)_2CO]$ compounds represent useful precursors in the synthesis of cyclopentadienones, quinones, hydroquinones, and pyrones.[7]

In order to obtain a deeper knowledge of the bonding scheme in this class of molecules, we decided to pursue the same strategy adopted in investigating the electronic structure of other polynuclear organometallic complexes,[3] joining UV-photoelectron (UV-PE) spectroscopy with quantum-mechanical calculations.

We report here the gas-phase UV-PE spectra of $M_2(CO)_6[(Et-C_2-Et)_2CO]$ (M = Fe (**1**), Ru (**2**)) together with theoretical results at an ab initio level on $Fe_2(CO)_6[(H-C_2-H)_2CO]$. Keeping in mind the complexity of the investigated molecule, we performed the ab initio calculations adopting the valence-only pseudopotential method[8] with a minimal basis set. This method has been successfully tested on (butadiene)tricarbonyliron by comparing our results[9a] with all-electron literature ones[9b] and has given satisfactory outcomes in other studies on the electronic structures of different classes of compounds.[3a,9a]

Experimental Section

Compounds **1** and **2** were prepared from the reactions of 3-hexyne with $Fe_3(CO)_{12}$ and $Ru_3(CO)_{12}$, respectively, according to the method reported in literature.[10] He I and He II excited PE spectra were measured on a Perkin-Elmer PS 18 spectrometer modified by the inclusion of a hollow-cathode discharge lamp giving high output of He II photons (Helectros Development). The spectrometer was connected on line with a MINC-23 computer (Digital Equipments) by an interface built in our laboratory. Data acquisition was carried out by several sweeps (5-10) over 500 distinct channels. Typical sweep times were 5-10 min. The ionization energy (IE) scale was calibrated by reference to admixed inert gases (Xe-Ar) and to the He $1s^{-1}$ self-ionization. A heated inlet probe system was used at 80-100 °C.

The ab initio LCAO-MO-SCF calculations were performed with the introduction of pseudopotentials[8] to deal with all core electrons on each atom. The basis set and the calculation procedure have been already described elsewhere (ref 3a and references therein).

All the numerical experiments were carried out by running the PSHONDO program[11] on a VAX 11/780 computer.

$Fe_2(CO)_6[(H-C_2-H)_2CO]$ geometrical parameters are not reported in the literature, so they were assumed from an X-ray structural determination of a related compound ($Fe_2(CO)_6[(CH_3-C_2-CH_3)_2CO]$)[4b] positioning the H atoms in the same directions of the methyl carbon atoms. Molecular symmetry refers to the C_2 symmetry point group. Gross atomic charges and bond overlap populations were obtained by Mulliken's population analysis.[12]

Results and Discussion

The electronic structure of the $Fe_2(CO)_6$ fragment has been already described qualitatively by Thorn and Hoffmann;[13] the interactions with the bridging organic fragment mainly involve its outermost occupied 1a and 1b levels as well as the low-lying vacant 2a, 2b, and 3a fragment MOs (see Figure 2). The frontier orbitals of the dienone ligand (L) are hardly described because its twisted conformation prevents proper discrimination between σ and π characters. However, in order to make easier the subsequent analysis of the ab initio results, assessing the predominant

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Table I. Pseudopotential ab Initio Results for $Fe_2(CO)_6(H–C_2–H)_2CO$

		population, %									partial overlap population					
		2 Fe														
MO	*E*, eV	s	p	d	6 CO	C_3	O_3	2 C_1	2 C_2	4 H	Fe–Fe′	C'_1–Fe	C_1–Fe	C'_2–Fe	C_1–C_2	dominant character
27a	−7.80	0	25	21	26	0	1	12	15	0	0.156	0.008	0.066	0.060	−0.068	Fe–Fe + π^*
26b	−10.92	1	4	7	3	5	38	18	24	0	−0.046	0.010	0.014	0.078	0.098	pseudo-π
25b	−11.70	0	6	1	1	3	60	7	16	6	−0.008	−0.018	0.036	0.014	−0.068	oxygen lone pair
26a	−11.71	0	5	10	3	0	0	38	39	5	−0.016	0.008	0.028	0.046	0.112	pseudo-π
24b	−12.65	1	6	13	4	0	12	51	7	6	−0.018	−0.052	0.208	0.004	−0.026	n^-
25a	−13.26	5	7	22	13	1	1	36	10	5	0.058	0.054	0.132	0.004	−0.016	n^+
24a	−14.18	0	0	82	14	0	1	1	1	1	−0.002	0.006	−0.008	−0.002	0.000	d pairs
23b	−14.26	0	1	77	14	2	3	1	1	1	−0.016	−0.004	0.008	0.002	−0.002	
22b	−14.59	0	1	55	11	8	7	2	11	5	0.004	0.016	0.000	0.008	0.000	
21b	−14.94	0	1	76	13	2	4	1	2	1	−0.014	0.006	−0.006	−0.008	−0.004	
23a	−15.03	1	1	44	10	3	12	16	11	2	0.022	0.008	0.040	−0.018	0.054	
22a	−15.05	0	0	60	8	1	5	9	9	8	0.016	0.004	−0.026	0.000	0.038	

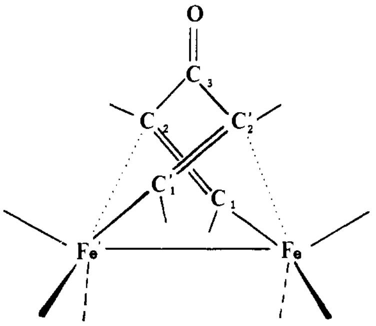


Figure 1. View of the iron "flyover-bridge" compound.

σ/π character (hereafter, pseudo-σ/π), we performed a qualitative calculation within the extended Hückel (EH) scheme on L with planar and twisted conformations (see Figure 2). On passing from the planar structure to the twisted one, we observe that the in-phase n^+ (2a MO) and out-of-phase n^- (4b MO) linear combinations of the radical lobes localized on C_1 carbon atoms become almost degenerate (HOMO and LUMO of twisted L, respectively). The reduced through-space interaction between the two lobes is certainly responsible for this effect. Furthermore, minor perturbations are present on virtual pseudo-π levels (see Figure 2). In the same figure the EH levels of the whole molecule are also reported. Significant variations, mainly due to the different L conformation, are present with respect to the energy level ordering obtained for $Fe_2(CO)_6[(H–C_2–H)_2CH_2]$ in the hypothetical C_{2v} geometry.[13] First of all, the favorable energy matching between the HOMO of $Fe_2(CO)_6$ and the LUMO of twisted L produces a dramatic stabilization of the n^- combination, giving rise to a MO almost degenerate with the n^+ one, which is stabilized by interaction with the 3a MO of the $Fe_2(CO)_6$ fragment. Moreover, the HOMO (representing a direct metal–metal bond) is now stabilized with respect to the parent orbital 1a in $Fe_2(CO)_6$ because it interacts via back-donation with the empty pseudo-π 3a orbital of the dienone fragment. It is interesting to point out that n^+ is not engaged in the aforesaid interaction because of the unfavorable overlap with the metal–metal bond.

In Table I the ab initio eigenvalues and the population percentage analysis of the 12 outermost MOs are presented together with some partial overlap populations (OPs) useful to describe the nature of each MO; moreover, relevant gross atomic charges and total OPs are reported in Figure 3.

The 27a HOMO is quite distinct in energy from the following MOs, and it is mainly localized on the iron atoms. It accounts for most of the Fe–Fe′ direct interaction (see its partial OP in Table I vs. the total OP in Figure 3) to which both 4p and 3d metal AOs contribute to a similar extent. Moreover, the localization of this MO on the organic fragment is significant and the eigenvector analysis confirms the back-bonding interaction (see the negative OP between C_1 and C_2 atoms) already proposed by the above EH results.

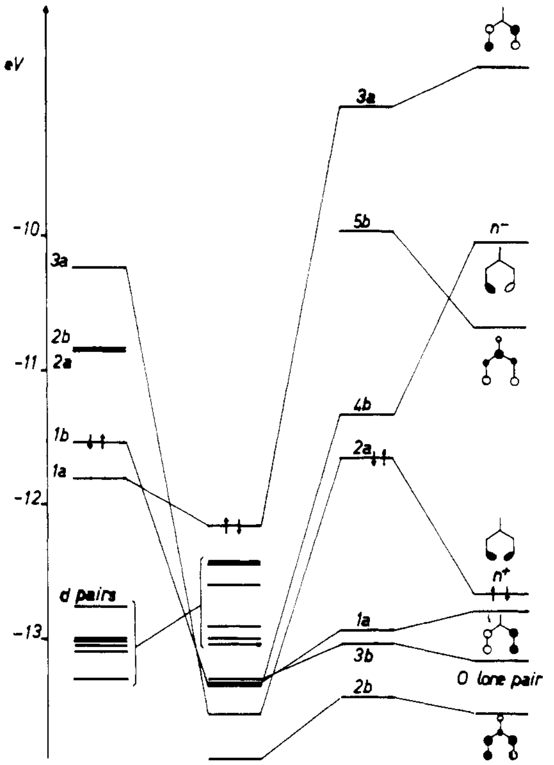


Figure 2. EH orbital interaction diagram. The four columns refer (from left to right) to $Fe_2(CO)_6$, $Fe_2(CO)_6[(H–C_2–H)_2CO]$, and $[(H–C_2–H)_2CO]$ in the twisted conformation and $[(H–C_2–H)_2CO]$ in the planar conformation.

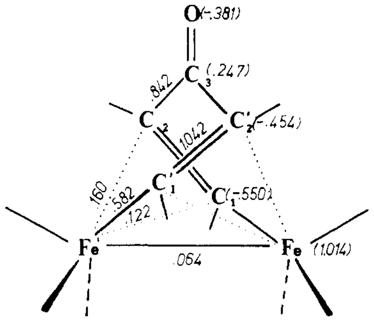
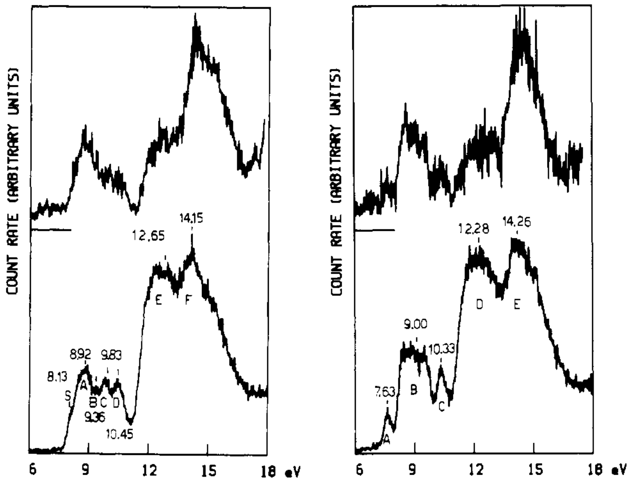


Figure 3. Relevant ab initio gross atomic charges (in parentheses) and overlap populations of $Fe_2(CO)_6[(H–C_2–H)_2CO]$.

The five MOs from 26b to 25a are mainly localized on the L fragment. Among them, the 25b MO has a lone-pair character localized on the ketonic oxygen, and it can be related to the fragment 3b MO. 24b and 25a MOs are respectively the n^- and n^+ combinations of radical lobes, strongly involved in the σ interaction between $M_2(CO)_6$ and L. The inspection of OPs of Table I and Figure 3 shows that most of the interaction between C_1 and Fe atoms is accounted for by these two MOs. The 26b and 26a orbitals represent the bond interactions between the filled pseudo-π



(1) (2)

Figure 4. He I and He II excited PE spectra of **1** and **2**. PE bands are labeled alphabetically.

orbitals of L and the iron atoms. The analysis of the relative eigenvectors shows that the most important contribution comes from the Fe–C'_2 atoms (see the OPs in Table I). This interaction is mainly σ in character; however, a π-type weak interaction between Fe and C_1 is also present for these MOs.

The six MOs (from 24a to 22a) with an atom-like character (d pairs) are grouped in a range of ca. 1 eV. The inner energy position of these MOs with respect to the ligand-based ones is a common feature of the ab initio molecular ground state for this class of molecules. However, one has to recall for the following discussion that the ionization processes relative to d pairs give rise to larger electronic reorganization.[14] Thus, the d-pair ionizations are commonly found at lower IE values than the ligand-based ones.

Some further insight into the electronic structure of the title molecules can be obtained by focusing our attention on the total OPs reported in Figure 3. First of all, we have to observe that the OPs relative to C'_2–Fe and C'_1–Fe (equal to 0.160 and 0.122 e, respectively) are much lower than the C_1–Fe one (0.582 e), pointing out that the main interaction between $M_2(CO)_6$ and L involves terminal carbon atoms and is essentially σ in character.

On the basis of the above discussion and by referring to the PE results of similar $M_2(CO)_6L$ derivatives,[3a,3b,15] we can now go on interpreting the PE spectra reported in Figure 4 for title molecules. No doubt at all exists in relating the bands labeled B, C, and D for **1** to ionizations from L-localized MOs because of their dramatic intensity decrease under the He II ionization source.[16] We propose to assign band B to the ionization from MO 26b while both bands C and D are associated with two ionizations, from 25b, 26a and from 24b, 25a, respectively.[18] The broad band A is to be related in turn, to ionizations from the six iron-like 3d pairs (24a, 23b, 22b, 21b, 23a, and 22a MOs), and shoulder S on its lower IE side is assigned with confidence to the HOMO (27a), which, as already pointed out, describes the direct metal–metal interaction.

The spectral region beyond 11 eV, consisting of two very broad and ill-resolved bands E and F, is mainly due to ionizations from MOs localized on the ethyl groups of the organic fragment (note the dramatic decrease in relative intensity of band E on passing from an He I to an He II ionization source) and to Fe–CO σ MOs and 1π CO levels.

Very interesting is the comparison of the PE spectra of **1** with those of the ruthenium analogue **2**. Actually the analysis of PE spectra of complexes with the same ligand and different isoelectronic metal atoms is a powerful tool for the assignment, because one can use well-known trends in the properties of the metal atoms (such as photoionization cross section and *n*d orbital energies).

If we keep in mind the smaller relaxation phenomena[19] undergone by 4d pairs with respect to the 3d ones, the assignment of the PE spectrum of **2** is straightforward. First of all, band A (related to the shoulder S in **1**) is now well resolved and it can be related to the ionization from the MO describing the direct Ru–Ru′ interaction. As a consequence of different relaxations undergone by 4d pairs with respect to the 3d ones, the six atom-like MOs strongly overlap in **2** with ligand-based MOs, giving rise to a less resolved He I spectrum. Assuming the same energy ordering found in the iron complex holds for the ruthenium one, we can tentatively assign the lower IE side of the broad band B to the ionization from the six ruthenium-like 4d pairs (24a, 23b, 22b, 21b, 23a, and 22a MOs) and the higher IE side to the ionizations from 26b, 25b, and 26a MOs. Finally, band C is assigned to the ionization from 24b and 25a MOs. Such an assignment is consistent with the decrease in relative band intensity shown by both band C and the higher IE side of band B under an He II ionization source.[16]

Conclusion

This paper confirms the capability of pseudopotential method to obtain, with relatively low computational effort, a detailed description, at the ab initio level, of the bonding scheme existing in molecules with two transition-metal atoms. The theoretical results clarify the role played by the bridging ligand and point out that the bonding between the "inorganic" and the "organic" moieties is mainly due to a σ interaction between metals and terminal carbon atoms; however, internal carbon atoms are also involved (to a smaller extent) through the pseudo-π MOs of the twisted L fragment.

From the study of the electronic structure of organometallic complexes containing dimerized alkynes as "flyover-bridge" $Fe_2(CO)_6[(R—C_2—R)_2CO]$, "ferrole" $Fe_2(CO)_6(RC_2R)_2$,[3a] and "μ-butatriene" $Fe_2(CO)_6(R_2C{=}C{=}C{=}CR_2)$[3b] we observe that the bonding between the metallic fragment and the organic moiety is always dominated by interactions σ in character. It is likely that this is due to the high conformational flexibility of the organic chains, which adopt suitable geometries in order to maximize the metal–ligand interactions and to improve the stability of the whole molecule. On the other hand, previous studies of the electronic structure of organometallic compounds having a single alkyne, μ_x-η^2 coordinated to the metallic framework (x = 2, 3, 4), such as $Ni_2(C_5H_5)_2(R—C_2—R)$,[3c] $Fe_3(CO)_9(R—C_2—R)$,[3d] and $Ru_4(CO)_{12}(R—C_2—R$,[3e] show that the dominant role in the overall interaction is played by the π-type metal → alkyne back-donation. Remarkably, these electronic features reproduce some chemical behavior: the μ_2-$\eta^2Co_2(CO)_6(R—C_2—R)$ class can be hydrogenated to the corresponding olefins under mild conditions at measurable rates; on the contrary, the isoelectronic "μ-butatriene" $Fe_2(CO)_6(R_2C{=}C{=}C{=}CR_2)$ complex does not react at all with H_2, even under more forced conditions.[20] The

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strong interactions between the butatriene chain and the $Fe_2(CO)_6$ fragment[3b] are certainly responsible for this lack of reactivity.

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Registry No. **1**, 67400-66-2; **2**, 99748-42-2; Fe, 7439-89-6; Ru, 7440-18-8.

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Cadmium-113 Nuclear Magnetic Resonance Spectroscopic Study of Mixed-Ligand Tetranuclear Clusters of the Type $[Cd_4(EPh)_x(E'R)_{10-x}]^{2-}$ and of the Mixed-Metal Clusters $[Cd_xZn_{4-x}(SPh)_{10}]^{2-}$

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The synthesis of $(Me_4N)_2[Cd_4(SePh)_{10}]$ (**1**) is described. The ^{113}Cd-enriched compound (**1***) undergoes ligand redistribution with the sulfur analogue (**2***) to give the series $[^{113}Cd_4(SPh)_x(SePh)_{10-x}]^{2-}$ (x = 0–10), in which each member is characterized by a single line in the 44.4-MHz ^{113}Cd NMR spectrum at ambient probe temperature. The same complexes can be made in solution by redox reaction of **1*** with Ph_2S_2 or **2*** with Ph_2Se_2. Similarly, at ambient probe temperature, resolvable single ^{113}Cd NMR lines characterize the species $[Cd_4(SPh)_x(SR)_{10-x}]^{2-}$ (R = Me, x = 8–10; R = Bu, x = 4–10; R = $PhCH_2$, x = 7–10; R = 2-C_6H_4Me, x = 0–10), produced from **2** or **2*** and R_2S_2, $[Cd_4(SePh)_x(SBu)_{10-x}]$ (x = 5–10), produced from **1** and Bu_2S_2, $[^{113}Cd_4(SPh)_x(TePh)_{10-x}]^{2-}$ (x = 8–10), produced from **2*** and Ph_2Te_2, and $[^{113}Cd_4(SePh)_x(TePh)_{10-x}]^{2-}$ (x = 7–10), produced from **1*** and Ph_2Te_2. The observed or extrapolated ^{113}Cd NMR chemical shifts of $[Cd_4(ER)_{10}]^{2-}$, in which the kernels are $(RE)Cd(\mu\text{-}ER)_3$, are close to those of $[Cd(ER)_4]^{2-}$, confirming that ^{113}Cd NMR is not very sensitive to the bridging/terminal nature of the bound groups, as found in earlier work. When mixtures of $[Cd_4(SPh)_{10}]^{2-}$ and $[Zn_4(SPh)_{10}]^{2-}$ were reinvestigated with use of ^{113}Cd enrichment, only three cadmium-containing species could be detected by ^{113}Cd NMR. These are probably $[^{113}Cd_xZn_{4-x}(SPh)_{10}]^{2-}$ (x = 2–4). The relevance of this nonstatistical metal distribution to that in zinc–cadmium metallothionein is discussed.

Introduction

The ^{113}Cd NMR spectra of ^{113}Cd-enriched cadmium and cadmium-containing mixed-metal metallothioneins have provided invaluable information about the spatial disposition of the cadmium ions in the binding sites of the cysteine-rich protein.[1,2] Thus, for intance, on this basis it is thought that mammalian cadmium metallothionein (Cd-MT) contains two types of polynuclear cadmium clusters, a three-atom cluster, $Cd_3(S\text{-cyst})_9$, and a four-atom cluster, $Cd_4(S\text{-cyst})_{11}$, while Cd-MT from the crab *Scylla serrata* contains two different three-atom clusters of the type $Cd_3(S\text{-cyst})_9$.

Mammalian MT induced by administration of cadmium always contains a significant amount of zinc (see, for examples, ref 1–3). The ^{113}Cd NMR spectrum of Zn,^{113}Cd-MT is more complex than that of ^{113}Cd-MT but can be interpreted[1,2] to show that the distribution of the two metals over the seven binding sites is not random, the overwhelming majority of ^{113}Cd occupying the four-atom cluster. An assumption in this interpretation is that replacement of cadmium by zinc in a particular cluster has relatively little effect on the ^{113}Cd NMR chemical shifts of the remaining ^{113}Cd nuclei.[1]

To our knowledge there is no simple model available for the three-atom cluster of MT. However, the tetranuclear cluster $[Cd_4(SPh)_{10}]^{2-}$ is well established,[4] and the zinc analogue is also known.[5] These clusters have structures based on an adamantane-like $M_4(\mu\text{-SPh})_6$ cage in which each metal ion is also associated with one terminal thiolate.[4,5] We[6] and others[7] have shown recently that 45-Hz two-bond $^{113}Cd\text{–}S\text{–}^{111}Cd$ nuclear spin–spin coupling is observable in the ^{113}Cd and ^{111}Cd NMR spectra of $[Cd_4(SPh)_{10}]^{2-}$, making this a good model for the 20–50-Hz $^{113}Cd\text{–}S\text{–}^{113}Cd$ couplings observed in the ^{113}Cd NMR spectra of various ^{113}Cd-MT's. In addition, the fine structure found in the $^{111/113}Cd$ NMR spectra of $[Cd_4(SPh)_{10}]^{2-}$ shows that the Cd_4 core of this species is long-lived on the $^{111/113}Cd$ NMR time scale. The ^{113}Cd NMR chemical shift of $[Cd_4(SPh)_{10}]^{2-}$ (e.g. in acetone at 295 ± 1 K, 575 ppm relative to external $Cd(ClO_4)_2(aq)$[6]) is outside the range reported for ^{113}Cd-MT, and better models for this parameter are desirable. No discrete clusters $[Cd_4(SR)_{10}]^{2-}$ (R = alkyl) have been reported, though Kurtz and co-workers[8] have drawn attention to the occurrence of related tetraatomic clusters within the structure of the decanuclear cluster $[Cd_{10}(SCH_2CH_2OH)_{16}]^{4+}$. In the solid-state ^{113}Cd NMR spectra of this 10-atom cluster, as the ClO_4^- and SO_4^{2-} salts, chemical shifts from 623 to 705 ppm were found for the CdS_4 kernels, depending on the particular salt and its extent of aquation, and it was concluded, inter alia, that disortions of the kernel, rather than differences in the number of bridging vs. terminal thiolates, affect the chemical shifts most significantly.[8]

In this paper we describe our ^{113}Cd NMR studies of various mixed-thiolate clusters $[Cd_4(SPh)_x(SR)_{10-x}]^{2-}$ in solution. We could find no previous report of such discrete cadmium-containing mixed-ligand clusters. As selenium has an important antagonistic effect toward cadmium toxicity,[9] we have extended our study to selenium-containing tetranuclear clusters, which we describe for

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