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Electronic structure of $\text{Ru}_3(\text{CO})_6(\text{CH}_3\text{C}=\text{CHCH}=\text{NC}_3\text{H}_7\text{-i})_2$ as indicated by UV-photoelectron spectroscopy and DV- $X\alpha$ quantum mechanical calculations

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Abstract

The electronic structure of a novel trinuclear open (or acyclic) cluster of ruthenium $[\text{Ru}_3(\text{CO})_6(\text{CH}_3\text{C}=\text{CHCH}=\text{NC}_3\text{H}_7\text{-i})_2]$, isolobal with ruthenocene, has been investigated by combining He I/He II gas phase UV photoelectron spectroscopy and Hartree–Fock–Slater first-principle discrete variational (DV-) $X\alpha$ calculations. The derived bonding scheme emphasizes the leading role played by a 3-center-2-electron interaction between the Ru atoms in determining the stability of the bent open metal core, in spite of the absence of any ligand bridging the peripheral ruthenium. Moreover, the bent arrangement of the open metal core has been calculated to be ca. 3 Kcal/mol more stable than the linear one.

Introduction

The electronic properties of polynuclear complexes containing a metallacyclic moiety have been the subject of several theoretical and experimental investigations [1–3], with the main objective being clarification of the bonding scheme within the metallacycle and of the role played by the metal–metal bond in modifying metal–ligand interactions [1a]. In this paper, which forms part of a comprehensive

Table 1

DV-X α results for Ru₃(CO)₆(CH₃C=CHCH=NCH₃)₂

Eigenvalue	MO	- ϵ (eV)	TSIE	Assign- ment	Population (%)											
					Ru		zRu'		2N ₁	2C ₂	4(CH)	4(CH ₃)	6(CO)			
					s	p	s	p								
38b ^a		3.03			0	0	4	5	5	24	11	9	5	2	35	
38a		5.31	7.46		4	2	61	0	4	9	2	2	6	2	8	
37b		5.90	8.04	A	0	0	69	0	0	11	5	5	2	2	6	
36b		6.22	8.11		0	0	22	0	5	27	9	11	2	4	20	
37a		6.59	8.51		3	2	24	1	7	12	10	9	16	6	10	
35b		6.67	8.60	B	0	1	3	0	1	23	17	13	25	5	12	
36a		6.89	8.94		1	0	61	3	6	12	1	2	4	0	10	
35a		7.11	9.13		0	0	6	0	1	49	2	11	7	2	22	
34b		7.31	9.24		0	0	3	0	4	38	9	11	9	6	20	
34a		7.34	9.37	C	0	0	1	1	5	52	5	5	2	3	26	
33b		7.50	9.57		0	0	1	0	0	65	1	2	6	2	23	
33a		7.58	9.63		0	0	2	0	1	65	1	0	4	2	25	
32b		7.80	9.95		0	0	1	0	1	28	18	13	12	10	17	
32a		8.17	10.32	D	0	0	10	0	2	6	21	20	14	16	11	
31a		8.93	11.08		1	0	7	1	1	27	3	25	10	14	11	
31b		9.05	11.20	E	0	0	7	0	1	27	4	21	11	16	13	
30b		9.58	11.73		0	0	1	0	1	8	31	1	33	17	9	
30a		9.74	11.90		0	0	2	1	2	9	36	4	20	13	13	

^a Lowest unoccupied MO.

Table 1 (continued)

MO	Eigenvalue	- ϵ (eV)	TSIE	Assign- ment	Orbital overlap population					character	
					Ru-Ru'	Ru'-C ₂	Ru-C ₂	Ru'-N ₁	Ru-N ₁		
38b ^a		3.03									
38a		5.31	7.46		-0.102	0.031	-0.061	0.027	-0.062	(4d-like) Ru	
37b	A	5.90	8.04		-0.105	0.006	0.049	0.002	-0.015	(4d-like) Ru	
36b		6.22	8.11		-0.021	0.004	0.018	0.034	-0.028	4d-like + π_3^-	
37a	B	6.59	8.51		0.017	0.033	0.132	0.051	0.092	4d-like + π_3^+	
35b		6.67	8.60		0.002	0.017	0.018	-0.040	0.048		
36a		6.89	8.94		0.288	-0.021	-0.012	-0.040	0.012	(4d-like) Ru	
35a		7.11	9.13		0.005	0.059	0.003	0.000	0.010	(4d-like) Ru'	
34b		7.31	9.24		0.028	0.080	-0.005	0.016	-0.006	(4d-like) Ru'	
34a	C	7.34	9.37		-0.009	0.008	-0.005	-0.018	0.015	(4d-like) Ru'	
33b		7.50	9.57		0.013	0.000	-0.001	-0.015	0.017	(4d-like) Ru'	
33a		7.58	9.63		0.003	-0.008	0.001	-0.009	0.000	(4d-like) Ru'	
32b	D	7.80	9.95		-0.004	0.073	0.015	0.089	-0.004	π_2^-	
32a		8.17	10.32		-0.032	0.099	0.020	0.090	0.011	π_2^+	
31a	E	8.93	11.08		0.069	0.202	0.091	0.012	0.024	n_C^+	
31b		9.05	11.20		0.063	0.174	0.086	0.022	0.051	n_C^-	
30b		9.58	11.73		0.016	-0.001	-0.006	0.124	0.015	n_N^-	
30a		9.74	11.90		0.024	0.037	0.003	0.190	0.043	n_N^+	

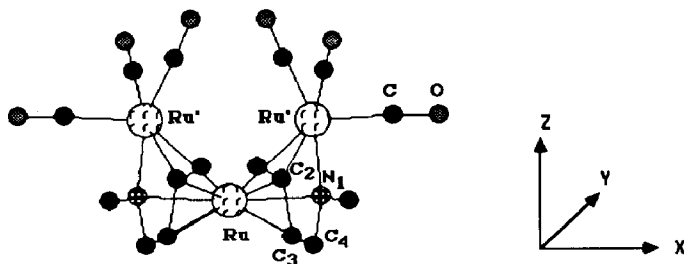


Fig. 1. Schematic structure of the trinuclear open (or acyclic) cluster $[\text{Ru}_3(\text{CO})_6(\text{CH}_3\text{C}=\text{CHCH}=\text{NC}_3\text{H}_7\text{-i})_2]$.

investigation of the electronic properties of polynuclear organometallic clusters [4], we report a combined theoretical and experimental study of the electronic structure of a novel trinuclear open (or acyclic) cluster $[\text{Ru}_3(\text{CO})_6(\text{CH}_3\text{C}=\text{CHCH}=\text{NC}_3\text{H}_7\text{-i})_2]$ (see Fig. 1, and denoted subsequently as RuMAD) combining He I/He II gas-phase UV photoelectron (PE) spectroscopy and Hartree–Fock–Slater first-principle discrete variational (DV-)X α calculations [5].

Experimental

Preparation. RuMAD is one of the products of the reaction between N-i-Pr-(*E*)-crotonaldimine with $\text{Ru}_3(\text{CO})_{12}$, as described in ref. 6.

Spectra. The He I/He II PE spectra were recorded on a Perkin Elmer PS-18 spectrometer modified by inclusion of a hollow-cathode discharge lamp giving high output of He II photons. The spectra were recorded in the 150–180 °C temperature range and were calibrated by reference to admitted inert gases (Xe–Ar) and the He $1s^{-1}$ self ionization. Depending on temperature, different amounts of free CO were detected (see the He II spectrum). However, the identical pattern of the spectra, both in relative intensities and position of the peaks, allowed us to neglect the possible presence of volatile species other than the title compound.

Computational details. Electronic structure calculations were carried out on a VAX8530 at the computing center of the University of Basilicata by the discrete variational (DV-)X α method [5].

Numerical atomic orbitals (AOs, through $5p$ on Ru, $2p$ on C, N, O and $1s$ on H) obtained for the neutral atoms were used as basis functions. Due to the size of the investigated system, orbitals $1s$ – $4p$ (Ru) and $1s$ on carbon, nitrogen and oxygen were treated as a part of a frozen core in the molecular calculations. Atomic orbital populations were computed by use of the Mulliken scheme [7]. More details about the used computational procedure can be found in ref. 8. Experimental and theoretical IEs were compared by use of the transition state (TS) procedure [9], which has been applied to each single MO reported in Table 1. For the exchange scaling parameter α , the Gaspar–Khon–Sham value [10] was used. Geometrical parameters for the title compound were taken from ref. 6 and idealized to C_2 symmetry. In order to save computer time, the electronic properties of the i-Pr substituents on nitrogen atoms were treated as methyl groups. Due to the low symmetry of the whole molecule, which in principle allows extensive mixing of AOs,

the character of selected molecular orbitals (MOs) was assigned by reference to the relative contour plots (CPs).

Results and discussion

The solid state structure of RuMAD (see Fig. 1) indicates the presence of two ruthena-azacyclopentadienyl rings [Ru'N(1)C(4)C(3)C(2)] [6], both of them isolobal with a η^5 -coordinated C_5H_5 fragment [11]. On this basis, the description of the electronic structure of the title molecule can be nicely worked out by taking advantage of the isolobality between RuMAD and the well known ruthenocene (subsequently referred to as RuCp₂). According to the closed valence (CV) MO theory, two metal-metal bonds are expected in RuMAD because of the presence of 50 CV electrons [12]. Such qualitative arguments agree well with crystallographic data [6], which indicate the presence of two very different metal-metal distances (Ru-Ru' = 2.704; Ru'-Ru' = 3.851 Å, see Fig. 1).

The He I/He II PE spectra of the title compound are reported in Fig. 2, where bands have been labelled alphabetically. The high ionization energy (IE) region (over 11 eV) consists of three broad bands F, G, H and a shoulder S on the lower IE side of band F. They are mainly due to the ionization from i-propyl σ MOs and carbonyl 1π , 5σ and 4σ levels. Analysis of this region is not relevant to this contribution and is not considered further. The low IE region (up to 11 eV) contains at least five overlapping bands (A, B, C, D and E). Consideration of many other ruthenium based organometallic clusters [1d,4] suggests that the IEs of the outer-

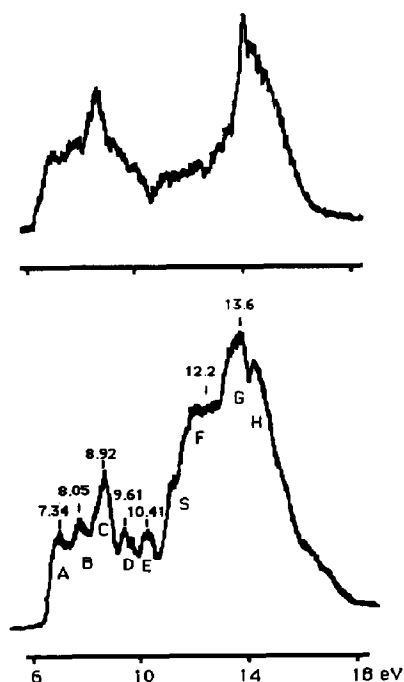


Fig. 2. He^I (below) He^{II} (above) PE spectra of RuMAD.

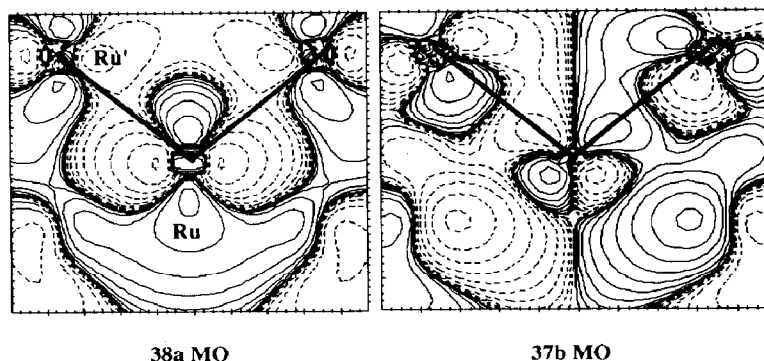


Fig. 3. DV- $X\alpha$ contour plot for the 38a HOMO and 37b MO in the XZ plane. Contour intervals are $5 \cdot 10^{-2}$ a.u. (nodes are not shown).

most ligand-based MOs, as well as levels mainly localized on the metal atoms (subsequently referred to as $4d$ -pairs), are expected in this energy region.

As already pointed out RuMAD is isolobal with RuCp_2 , whose electronic structure has been investigated both experimentally and theoretically [13]. In particular, He I/He II UV-PE results indicated, at the lowest IEs, the presence of a well defined band with a shoulder on the higher IE side [13b]. The band envelope was assigned to the ionizations from MOs strongly localized on the metal atom (e_{2g} and a_{1g} , assuming a staggered conformation with D_{5d} symmetry) [13b-e, 14*]. The e_{2g} pair is weakly Ru-Cp bonding in character while the a_{1g} pair is essentially non-bonding [13f]. On passing from RuCp_2 to RuMAD we can expect that the lower symmetry and the presence of the Ru-Ru' interaction will significantly perturb levels reminiscent of the e_{2g} and a_{1g} ones. Furthermore, MOs mainly localized on the Ru'(CO)₃ fragments as well as nitrogen lone pairs will further complicate the PE pattern in the low IE region with respect to that for RuCp_2 .

The eigenvalues and the charge density analysis of the outermost MOs of RuMAD obtained by DV- $X\alpha$ calculations are reported in Table 1 together with selected Orbital Overlap Populations (OOPs). The theoretical results agree quite well with the aforesaid qualitative analysis even though, as already pointed out, the low symmetry of the complex, coupled with the direct Ru-Ru' interaction, tends to complicate the simple bonding scheme based on the isolobality with RuCp_2 . For example, the 38a HOMO and 37b MO, which represent the levels related to the e_{2g} orbital in RuCp_2 (they are mainly localized on Ru, see Table 1 and Fig. 3), have a quite strong Ru-Ru' antibonding character (see relative OOPs). Moreover, the 36a MO (the relative CP is reported in Fig. 4) which is related to the RuCp_2 metal based a_{1g} level (the $4d$ contribution is only due to the Ru $4d_{z^2}$ AO), is here significantly more stable than the 38a and 37b MOs (see Table 1). Such a stabilization can ultimately be traced to the strong Ru-Ru' bonding character of this orbital. Actually, most of the Ru-Ru' direct interaction is accounted for by this level; the relative OOP is 0.288e (the largest among the occupied levels) while the total Ru-Ru' OP is 0.260e. This strong interaction may be rather surprising because of the non-bonding nature, in RuCp_2 , of the a_{1g} level (see above). On the other hand,

* Reference number with asterisk indicates a note in the list of references.

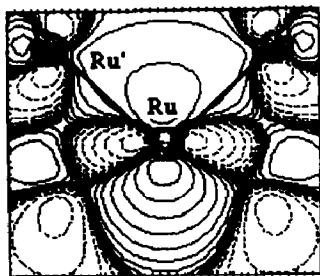


Fig. 4. DV-X α contour plot for the 36a MO in the XZ plane. Contour intervals are $5 \cdot 10^{-2}$ a.u. (nodes are not shown).

in the present case, the Ru $4d_{z^2}$ AO can interact with suitable combinations of Ru' $4d$ levels (see Fig. 4) to give rise to a Ru'-Ru-Ru' 3-center-2-electron bond.

More insight into the electronic structure of the title molecule can be gained by analyzing the metal-ligand interaction. In particular, the charge density analysis shows a higher participation of Ru' metal atoms in the 31a and 31b MOs [15*] (the symmetric and antisymmetric linear combinations of lone pairs of C₂ atoms, respectively) than in the 30a and 30b levels (the symmetric and antisymmetric linear combinations of lone pairs of N₁ atoms, respectively). Such a result indicates that the C₂-Ru' σ interaction is stronger than the N₁-Ru' one (see in Table 1 differences in the relative OOPs), in agreement with the different electronegativities of C₂ and N₁.

As far as the metal-ligand π interaction is concerned, it is useful to refer once more to the isolobality of RuMAD with RuCp₂. In the latter compound, we have 18 electrons (six from each C₅H₅⁻ and six from Ru²⁺), which are accommodated in the bonding Cp based and non-bonding ruthenium based MOs. The first question to be answered is related to the way in which the central Ru atom in RuMAD formally transfers two electrons into the Ru'-N(1)-C(4)-C(3)-C(2) rings, treated as two diheteracyclopentadienyl fragments η^5 -coordinated to Ru. The analysis of Table 1 indicates that the MOs responsible for such a transfer are the 36b and 37a levels (π_3^- and π_3^+ in Table 1, respectively). These orbitals, together with the 32b and 32a ones (π_2^- and π_2^+ in Table 1, respectively), represent the orbitals corresponding to the e_{1g} and e_{1u} MOs in the RuCp₂. Moreover, the charge density analysis indicates that the π_2 level poorly interacts with the central Ru atom. Accordingly, this results in the Ru atom being significantly more positive than the Ru' atoms (0.65 vs. 0.52). No character has been assigned to the 35b MO in Table 1 because the extensive AO mixing does not allow assignment of a specific nature to this level.

Before proceeding with the analysis of PE data, it is relevant to say something about the bent configuration experimentally determined for the open metal core. In this connection, a series of extended Hückel type calculations [16*] has been carried out in order to explore the effect of the simple rotation of one ruthena-azacyclopentadienyl ring with respect to the rest of the molecule. Our calculations indicated a delicate balance of forces behind the choice of a particular conformation. Direct Ru-Ru' interaction appears to favour a linear arrangement of the metal core, but in the bent one there is definitely a stronger bond between Ru and nitrogen atoms. As

a whole, a slight preference of ca. 3 Kcal/mole has been calculated for the bent geometry with respect to the linear one.

As far as PE data are concerned, the agreement between experimental and theoretical IEs is satisfactory; in fact, theoretical absolute values are overestimated by some 0.5–1.0 eV, whereas experimental IE differences are well reproduced. On the basis of relative intensity in the He I spectrum, we assign both band A and B to three ionization events each, namely band A to the ionizations from 38a, 37b, 36b MOs and band B to 37a, 35b and 36a levels. Band C is assigned as a whole to the ionizations from the remaining five levels (35a–33a in Table 1) strongly localized on the Ru' atoms and mainly responsible of back donation into CO based virtual levels. Finally both band D and E are assigned to two ionization events (32b–31b MOs). The proposed assignment is consistent with the spectral pattern obtained by using the more energetic He II radiation. In particular, both band D and E, mainly due to the ionization of ligand based MOs, show a dramatic decrease in relative intensity on passing from the He I to the He II ionization source (see Fig. 2) [17*].

Conclusions

DV-X α calculations indicate that the use of the isolobal analogy between RuCp₂ and RuMAD is a good starting point for the analysis of the bonding scheme of the latter compound. The theoretical analysis indicates that, as far as the Ru'-ligand σ bond within the diheteracyclopentadienyl fragments is concerned, the C₂-Ru' interaction is definitely stronger than the N₁-Ru' one. Moreover, two levels (36b and 37a MOs) are found to be responsible for the charge transfer from the central Ru atom into the partially occupied π_3 levels of the Ru'-N(1)-C(4)-C(3)-C(2) rings [19*]. Finally, the π_2 ligand based orbital seems to interact rather weakly with Ru.

As far as the stability of the bent open metal core in spite of the absence of any ligand bridging the Ru', theoretical results assign a leading role to the 36a MO, which looks like a 3-center-2-electron bond. Moreover, the bent arrangement of the open metal core is calculated to be ca. 3 Kcal/mole more stable than the linear one.

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- 14 In most metallocenes ring rotation probably occurs rather easily, but a D_{5d} point symmetry is usually adequate for the analysis of PE spectra.
- 15 The nature of a particular MO has been assigned by making reference to the relative CP.
- 16 Extended Hückel Parameters were taken from ref. 2a.
- 17 In fact on the basis of Gelius model [18], we expect a marked decrease in the cross section ratio $\sigma(C_{2p})/\sigma(Ru_{4d})$ on passing from the He I to the He II ionization source.
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- 19 It is worthwhile to remind that the $(CO)_3Ru'-N(1)-C(4)-C(3)-C(2)$ ring is isolobal to a C_5H_5 fragment, whose π_3 level is only half occupied.