Ab Initio Study of the Photoelectron Spectra and Bonding in $[Ru_2(O_2CH)_4]$ and $[Ru_2(O_2CH)_4(NO)_2]$: The Effect of Axial Ligands on Metal-Metal Interactions†

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Ab initio calculations at the self-consistent field level have been carried out on $[Ru_2(O_2CH)_4]$ and $[Ru_2(O_2CH)_4(NO)_2]$. The ground-state configuration of $[Ru_2(O_2CH)_4]$ is predicted to be $\sigma^2\pi^4\delta^2\delta^{*2}\pi^{*2}$ with the $\sigma^2\pi^4\delta^2\pi^{*3}\delta^*$ configuration being 15 kcal mol^{-1} higher in energy. The metal ionization energies of both molecules have been calculated by a configuration-interaction method and provide an interpretation of the experimental photoelectron spectra consistent with measured intensity changes using He I and He II radiation.

Since the identification of direct metal-to-metal double,[1] triple,[2] and quadruple[3] bonds in dirhenium systems in the early 1960s a great deal of effort has been put into understanding this important class of complex. A number of reviews on the subject have been published.[4] The quadruple bond was proposed by Cotton on purely qualitative grounds[3] to derive from a $\sigma^2\pi^4\delta^2$ configuration with maximal overlap between *d*-orbitals on the two metal centres. The σ bond is formed from overlap of the d_{z^2} orbitals on the two centres, the two π bonds by overlap of d_{xz} and d_{yz}, the δ bond formed by overlap of d_{xy} orbitals (the co-ordinate frame is usually considered with the metal atoms lying along the *z* axis), and the metal $d_{x^2-y^2}$ orbitals forming metal–ligand bonding orbitals. This scheme has been confirmed theoretically in the $[Re_2Cl_8]^{2-}$ complex by crystal-field theory and MS-Xα methods,[5] from extended-Hückel molecular orbital (EHMO) calculations[6] and *ab initio* self-consistent field (SCF) methods.[7] From this extensive set of calculations it has been shown that, in agreement with the qualitative schemes,[3] the σ bond is strongest, the π slightly weaker, and the δ being considerably weaker still. This ordering is obtained from the calculations by the overlap of the atomic orbitals on the two metal centres and also in Hay's generalized valence bond (GVB) calculations[7] by the occupation number of the antibonding component of the GVB pair.

In terms of metal–metal bonds the transition metals of the second and third rows show a greater propensity to form multiple bonds than their first-row analogues. This is usually rationalized by the observation that the 4*d* and 5*d* orbitals have a greater radial extent than the 3*d* orbitals.[8] Complexes containing metal–metal bonds between first-row metals are also much more sensitive to the nature of bridging and axially bonded ligands. Chromium provides perhaps an extreme example of short[9] and long[10] metal–metal bonds. The corresponding second- and third-row complexes are much less sensitive.[4a,11–13] The longer chromium–chromium bond lengths occur in complexes with tetra-μ-carboxylate bridging ligands. These ligands have proved very useful in the study of this class of complex, first characterized in 1953,[14] since they allow the metal–metal interaction to extend over a wide range of separations.[15]

We now present a brief discussion of previous experimental and theoretical studies on metal–metal bonded species of relevance to the diruthenium carboxylate complexes, to be followed by a report of our calculations for the complexes $[Ru_2(O_2CH)_4]$ and $[Ru_2(O_2CH)_4(NO)_2]$.

Previous Studies of Metal–Metal Bonds in Diruthenium Complexes

The late transition-metal complexes of general formula $[Ru_2(O_2CR)_4L]$ have been the subject of a number of studies particularly with regard to catalytic activity.[16] The first such complex was synthesized by Stephenson and Wilkinson[17] in 1966 for R = Me, Et, or Pr^n. The magnetic data for this complex are consistent with three unpaired electrons in these molecules. (Magnetic moments of the second- and third-row transition metals show that almost all are low spin due to the higher spin–orbit interactions in these heavier elements.[8]) Stephenson and Wilkinson suggested that no direct metal–metal bond was present in the diruthenium complex due to the long metal–metal bond in presumably isostructural $[Cr_2(O_2CR)_4L_2]$[18] and $[Cu_2(O_2CR)_4L_2]$[14] species. This $[Cr_2(O_2CR)_4L_2]$ structure has subsequently been shown to be inaccurate with a revised chromium-chromium separation of 2.362 Å.[19]

The crystal structure and a bonding analysis of tetra-μ-butyrato-diruthenium chloride was published by Bennett *et al.*[15a] and revealed a very short ruthenium–ruthenium separation (2.281 Å) compared with ≈2.65 Å in the metallic element.[20] They postulated a ruthenium–ruthenium bond of order 3.5 arising from the electronic configuration $\sigma^2\pi^4\delta^2\delta^*\sigma_n\sigma_n^*$ which, assuming that the δ* and the two σ_n orbitals (combinations of the metal $5p_z$ orbitals) are close in energy, accounted for the observed three unpaired electrons.

However the σ_n and σ_n^* orbitals, which are essentially metal–metal non-bonding, have subsequently been shown to be inaccessible.[21] Magnetic and electrochemical properties of the tetra-μ-butyrato-diruthenium chloride complex have also been reported.[22,23]

Norman and co-workers[24,25] have presented a theoretical study of $[Ru_2(O_2CH)_4]^+$, $[Rh_2(O_2CH)_4]^+$, and related species and conclude that $[Ru_2(O_2CR)_4]$ has a . . . $\pi^{*3}\delta^*$ ground state with the . . . $\delta^{*2}\pi^{*2}$ state being only 2 kcal mol^{-1} higher in energy. They also discussed the influence of axial ligands on the ordering of the metal-localized molecular orbitals (m.o.s). Thus, in $[Rh_2(O_2CMe)_4X_2]$ a rhodium–rhodium single bond arising from the configuration $\sigma^2\pi^4\delta^2\delta^{*2}\pi^{*4}$ was proposed,[24,26] where the ordering is unaltered from that due to metal–metal interactions alone.[27] However, an extreme example of axial

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† *Non-S.I. units employed:* cal = 4.184 J, eV ≈ 1.60 × 10^{-19} J, a.u. = 2626 kJ mol^{-1}.

Table 1. Geometrical parameters used in the calculations for $[Ru_2(O_2CH)_4]$ and $[Ru_2(O_2CH)_4(NO)_2]$

Parameter	$[Ru_2(O_2CH)_4]$	$[Ru_2(O_2CH)_4(NO)_2]$
Ru–Ru/Å	2.276	2.532
Ru–O/Å	2.073	2.059
C–O/Å	1.242	1.246
C–H/Å	1.085	1.085
Ru–O–C/°	116.0	119.3
O–C–O/°	129.0	129.2
Ru–N/Å		1.815
N–O/Å		1.113
Ru–N–O/°		180

ligand bonding is found in $[Ru_2(C_{22}H_{22}N_4)_2]^{n+}$ {$(C_{22}H_{22}N_4)$ is a tetramethyldibenzo[*b,i*][1,4,8,11]tetra-azacyclotetradecinate-(2 –) ligand},[28] where a large reorganization in the ordering of the metal–metal m.o.s occurs.

As far as diruthenium complexes are concerned, confirmation of the ground-state neutral configuration was subsequently shown by Berry *et al.*[29] in the $[Ru_2(mhp)_4]$ complex (Hmhp = 6-methyl-2-hydroxypyridine) where a ruthenium–ruthenium configuration of $\sigma^2\pi^4\delta^2\pi^{*3}\delta^*$ was demonstrated by the assigned photoelectron (p.e.) spectrum.

Further complexes of the $[Ru_2(O_2CR)_4L]$ type have been prepared with R = H and L = Cl or Br; R = Me and L = Cl, Br, I, SCN, NO_3, or $MeCO_2$; R = Ph and L = Cl or Br.[30] All of these complexes possess three unpaired electrons and are assumed to be isostructural. Further studies by the Japanese group have been published[31] as well as by Cotton's group[11e] and also by Wilkinson's group.[12,13,32] The complexes prepared by Wilkinson and co-workers all have an even number of valence electrons and a core structure $[Ru_2(O_2CR)_4]^{n+}$ (n = 0 or 2). The authors suggest that their data are consistent with the $\pi^{*3}\delta^*$ configuration. The crystallographic data on $[Ru_2(O_2CR)_4L_2]$ species[12,13] are consistent with a double bond between the ruthenium atoms and no evidence of Jahn–Teller distortions is evident. An interesting derivative, L = NO, has also been prepared and is diamagnetic, arising presumably from the $\sigma^2\pi^4\delta^2\delta^{*2}\pi^{*4}$ configuration with the nitrosyl 2π orbitals interacting with the metal–metal π^* orbital. The lengthening of the ruthenium–ruthenium bond to 2.515 Å in the L = NO complex from 2.276 Å in the L = tetrahydrofuran (thf) complex is also indicative of the reduction in formal bond order from two to one.

The recent synthesis of $[Ru_2(O_2CR)_4L_2]$ complexes[12,13] and subsequent measurement of their p.e. spectra[33] affords an opportunity to study these new complexes from a theoretical viewpoint.

Computational Details

Our theoretical study of the $[Ru_2(O_2CH)_4L_2]$ complexes falls into two broad areas. First we present a study of the bonding in the ground state by SCF calculations and secondly describe calculations of the valence ionization energies (i.e.s) and assignment of the experimental p.e. spectra. From the discussion above on the description of metal–metal bonds it can be argued that the more multiple-bond character a metal–metal interaction possesses the more important electron-correlation effects become, although this effect may be due to the often shorter bonds inherent in multiply bonded systems. In addition, the lighter metals such as chromium, for example, require a highly correlated description whereas the experimental data for dimolybdenum complexes can be assigned at least qualitatively merely by SCF calculations. Both of these effects suggest that a qualitative bonding study on diruthenium species should be successful from SCF level calculations.

Our calculations were performed on the $[Ru_2(O_2CH)_4]$ and $[Ru_2(O_2CH)_4(NO)_2]$ complexes. Geometries for the two species were generated as follows. For the unligated complex the experimental geometry for $[Ru_2(O_2CMe)_4(thf)_2]$[12] was used since thf is a weakly donating ligand. The calculations on the $[Ru_2(O_2CH)_4(NO)_2]$ complex were performed with the experimental $[Ru_2(O_2CCF_3)_4(NO)_2]$ geometry.[13] In both cases the bridging groups were simplified to their O_2CH analogues with a C–H bond length of 1.085 Å.[34] The geometries of both complexes were idealized to D_{4h} point-group symmetry and the resulting geometrical parameters summarized in Table 1. The axial nitrosyl ligands were taken to be co-linear with the ruthenium–ruthenium axis for experimental[13] as well as empirical reasons.[35]

The all-electron *ab initio* calculations were performed with a basis of at least double-zeta quality for the valence orbitals. For ruthenium a *15s9p8d* primitive set of Gaussian functions[36] was contracted to *6s4p4d* by explicit calculation of the ruthenium d^8 neutral atomic configuration. For carbon, nitrogen, and oxygen *9s5p* primitive sets were contracted to *3s2p* with a *5s* hydrogen set contracted to *2s*.[37] Basis sets of this size have been shown to be of adequate flexibility in describing such systems[38–42] although smaller basis sets have been used successfully.[34,43,44] The Cartesian set of six *d*-type functions was used throughout giving 200 and 236 contracted basis functions for $[Ru_2(O_2CH)_4]$ and $[Ru_2(O_2CH)_4(NO)_2]$ respectively.

The SCF calculations on both species were carried out using restricted Hartree–Fock methods for closed and open shells. The $[Ru_2(O_2CH)_4]$ complex was studied in both $\sigma^2\pi^4\delta^2\pi^{*3}\delta^*$ and $\sigma^2\pi^4\delta^2\delta^{*2}\pi^{*2}$ states since SW-Xα calculations have predicted that the former state is only 2 kcal mol^{-1} lower in energy than the latter in $[Ru_2(O_2CH)_4]$.[25] The SCF calculations were improved with the addition of a two-term GVB pair taking into account the left–right correlation of the pair of σ electrons. This should lead to a more 'correct' description although this GVB calculation was not possible for the $\sigma^2\pi^4\delta^2\pi^{*3}\delta^*$ state.

The history of the development of p.e. spectroscopy in chemistry has been reviewed[45] with applications to mono- and bi-nuclear complexes discussed by Veillard and Demuynck[46] and for early studies by Cowley.[47] The combined use of p.e. spectroscopy coupled to *ab initio* or at least semiempirical methods has been advocated by Fenske[48] and Mulliken.[49] The usefulness of p.e. spectroscopy has been eloquently summed up by Cotton and Walton[4a] '. . . PES provides the most direct and unequivocal source of experimental information about the valence electrons in molecules.'

Due to the failure of Koopmans' theorem[50] to provide even qualitative estimates of ionization energies in many organometallic complexes[51–54] the calculation of the outer valence i.e.s was carried out using the multireference Koopmans' theorem single-excitation method (MRKTSE[55]). The MRKTSE method attempts to gain more accurate i.e.s than the ΔSCF[56–58] method but without the expense of a full ΔSCF plus configuration interaction (c.i.) procedure. The MRKTSE method recovers most of the relaxation energy associated with ionization but also includes some of the correlation effects that are different for the different ion states. The method involves a multireference c.i. expansion built from a set of Koopmans' theorem configurations (one electron ionized from each occupied m.o.) constructed from the ground-state m.o.s and then used to generate all single excitations from these configurations to a given set of virtual orbitals. This expansion may then be written as[42] equation (1)

$$\Psi^+_{\mathrm{MRKTSE}} = \sum_i c_i\Psi^+_i + \sum_{ikl} c_{ikl}\Psi^+_{i,k\to l} \qquad (1)$$

Table 2. Calculated atomic populations and energies for $[Ru_2(O_2CH)_4]$ ($^3A_{2g}$ and ^3E_u states) and $[Ru_2(O_2CH)_4(NO)_2]$ ($^1A_{1g}$)

	$[Ru_2(O_2CH)_4]$		$[Ru_2(O_2CH)_4(NO)_2]$
	$^3A_{2g}$	^3E_u	$^1A_{1g}$
Ru *s*	8.26	8.26	8.27
p	18.01	18.01	18.02
$4d_{z^2}$	1.02	1.01	1.06
$4d_{xz}$	1.53	1.77	1.60
$4d_{yz}$	1.53	1.77	1.60
$4d_{x^2-y^2}$	0.48	0.48	0.43
$4d_{xy}$	2.01	1.57	2.00
Charge/e	+1.17	+1.15	+1.02
O *s*	3.82	3.82	3.82
p	4.74	4.73	4.77
Charge/e	−0.56	−0.55	−0.59
C *s*	3.10	3.10	3.10
p	2.56	2.57	2.52
Charge/e	+0.34	+0.33	+0.38
H *s*	0.81	0.80	0.82
Charge/e	+0.19	+0.20	+0.18
N *s*			3.72
p			3.02
Charge/e			+0.26
O *s*			3.88
p			4.17
Charge/e			−0.05
E(SCF)/a.u.	−9 622.3926	−9 622.3686	−9 880.7983
E(GVB)/a.u.	−9 622.4466		−9 880.8460

where ψ^+_i are the Koopmans' theorem configurations and $\psi^+_{i,k\rightarrow l}$ are the single excitations from these states. The small correlation correction which occurs with the MRKTSE method arises from the fact that single excitations from one Koopmans' theorem configuration correspond to a double excitation from another such configuration. The reason why single excitations from the Koopmans' theorem states ψ^+_i allow relaxation to occur is discussed in appendix 3 of ref. 59 where it can be seen to be an extension to the ΔSCF method.

With the MRKTSE method the whole manifold of ionized states can be calculated because all states are mutually orthogonal. A second advantage of this method is that for molecules with two equivalent metal atoms the MRKTSE wavefunction can adequately describe the positive hole localization which may occur upon ionization, which is a noted failure of the ΔSCF method for these types of system.[60–62] This localization can be shown to arise from single excitations from pairs of reference configurations associating the bonding and antibonding counterparts in the description of the localized molecular orbitals. It is therefore necessary to include all the ionized states irrespective of symmetry, as reference configurations.

With these considerations in mind the c.i. expansion used for these calculations included (*i*) those Koopmans' theorem configurations generated from the GVB pair wavefunction which correspond to ionization of valence electrons from the Ru_2^{4+} moiety, and (*ii*) single excitations from these Koopmans' theorem configurations involving the filled metal–metal bonding and antibonding m.o.s and the low-lying virtual orbitals. These c.i. calculations included 78 and 97 virtual orbitals for $[Ru_2(O_2CH)_4]$ and $[Ru_2(O_2CH)_4(NO)_2]$ respectively. The virtual orbital cut-off was selected at an orbital eigenvalue of + 1.8 a.u. for both cases and should include all the relevant virtual orbitals describing the metal–metal relocalization configurations. This c.i. expansion is thus designed purely to describe the metal–metal interaction and so no attempt was made to describe the higher-energy ligand ionizations.

All calculations were performed with the GAMESS program[63] with the c.i. calculations performed by the method of Saunders and van Lenthe.[64] The calculations for the unligated complex were performed on the Cyber 205 of the University of Manchester Regional Computer Centre and for the nitrosyl complex on the Cray XMP/48 computer of the S.E.R.C. Rutherford Appleton Laboratory.

Results

The Ground State of $[Ru_2(O_2CH)_4]$.—The calculated atomic populations for the two possible states of $[Ru_2(O_2CH)_4]$, hereafter denoted as (**1**), are given in Table 2. The two states are formally $\sigma^2\pi^4\delta^2\pi^{*3}\delta^*$ (^3E_u) and $\sigma^2\pi^4\delta^2\delta^{*2}\pi^{*2}$ ($^3A_{2g}$) with the 4*d* orbital populations demonstrating these configurations. The energies from single-determinant SCF calculations on these two states which predict the ground state to be $^3A_{2g}$ are given in Table 2 along with the two-term GVB energy for the $^3A_{2g}$ state. The characters of the valence m.o.s of the two states are given in Table 3 ($^3A_{2g}$) and Table 4 (^3E_u).

The manifold of orbitals deriving mainly from the bridging ligands can be seen to be similar to those of $[Mo_2(O_2CH)_4]$,[34] although the orbitals have greater metal character in the diruthenium complex than in the dimolybdenum analogue. This is particularly so for the $1b_{1u}$ and $4e_u$ orbitals, the former having metal–metal δ* character and the latter significant π character.

The metal–metal bonding orbitals in the $^3A_{2g}$ state of $[Ru_2(O_2CH)_4]$ are the $2b_{2g}$ of δ symmetry, the $4a_{1g}$ of σ, the $2b_{1u}$ of δ*, and the $4e_g$ of π* symmetry. The lowest unoccupied molecular orbital (l.u.m.o.) is the σ* orbital ($3a_{2u}$). The $5e_u$ orbital has less metal character than the $4e_u$, but has a greater metal–metal bond overlap population, with the $4e_u$ possessing greater metal–bridge interaction. Similarly the $2b_{1u}$ is the δ* orbital possessing greater metal–metal character than the $1b_{1u}$.

Bond-overlap populations show that the metal–metal interaction is strongly bonding with contributions from the σ and π orbitals. The δ contribution is essentially non-bonding due to the occupancy of the bonding and antibonding components of the δ interaction. Addition of the GVB σ/σ* pair to this SCF description decreases the metal–metal overlap significantly with the pair energy of 0.054 a.u. (1.47 eV). This value is larger than the corresponding σ-orbital pair energy in $[Mo_2(O_2CH)_4]$ of 0.037 a.u.[34]

The bonding in the ^3E_u state is significantly different from that in the ground ($^3A_{2g}$) state. The carboxylate levels are essentially the same as in the ground state with those orbitals possessing significant metal *d* population having slightly more negative orbital eigenvalues than in the $^3A_{2g}$ state. For example the $3b_{1g}$ and $4e_u$ orbitals are 0.1 and 0.4 eV lower respectively. The $4e_u$ orbital has a greater metal *d* population in the ^3E_u state than in the $^3A_{2g}$ and is considered to be the formal metal–metal π-bonding orbital with a significantly greater metal–metal bond-overlap population than in the $^3A_{2g}$ state. The $2b_{2g}$ orbital is again the δ orbital with the $4a_{1g}$, $2b_{1u}$, $4e_g$, and $3a_{2u}$ being the σ, δ*, π*, and σ* orbitals respectively. These latter four orbitals all have somewhat greater metal populations than those in the $^3A_{2g}$ state.

The bond-overlap populations for the ^3E_u state all show that the metal–metal bonding is considerably weaker in this state than in the $^3A_{2g}$. This is associated with the increased population of the π* orbital in the ^3E_u state. In contrast, the reduction in δ* occupancy does little to enhance the bonding

Table 3. Valence molecular orbitals from the $\sigma^2\pi^4\delta^2\delta^{*2}\pi^{*2}$ SCF wavefunction for $[Ru_2(O_2CH)_4](^3A_{2g})$

		Orbital character (%)							
M.o.	*E*/eV	Ru(*s*)	Ru(*p*)	Ru(*d*)	O(*s*)	O(*p*)	C(*s*)	C(*p*)	H(*s*)
$3a_{2u}$	−0.33	16		79		5			
$4e_g$	−7.13			98		2			
$2b_{1u}$	−11.55			52		48			
$5e_u$	−12.59			44	1	45	2	2	7
$4a_{1g}$	−12.59	10	1	70		10		4	4
$1a_{1u}$	−12.97					100			
$3e_g$	−13.53					100			
$2b_{2g}$	−13.55			83		8		9	
$4e_u$	−14.17		1	50		27	3	8	12
$2e_g$	−14.20			2	1	97		1	
$2b_{2u}$	−14.53			4	3	90		3	
$2a_{2u}$	−14.64			3	2	92		2	
$3b_{1g}$	−14.74			17	1	51	3	7	21
$3a_{1g}$	−14.99	1		19	1	49	4	8	18
$1b_{1u}$	−16.11			49		51			
$1a_{2g}$	−17.43					69		31	
$3e_u$	−18.06					68		31	1
$1b_{2g}$	−19.28			17		58		24	
$1e_g$	−19.28		1	1	12	65		21	
$1b_{2u}$	−20.06			16	8	56		20	
$2b_{1g}$	−20.08				14	51	2	29	4
$1a_{2u}$	−20.33	7		5	9	59		20	
$2a_{1g}$	−20.34	1		1	13	50	1	30	4
$2e_u$	−20.48			7	14	50	2	23	4
$1e_u$	−23.51				13	28	25	16	18
$1b_{1g}$	−23.92			8	12	24	27	12	16
$1a_{1g}$	−24.13	4		3	12	27	28	13	14

Table 4. Valence molecular orbitals from the $\sigma^2\pi^4\delta^2\pi^{*3}\delta^*$ SCF wavefunction for $[Ru_2(O_2CH)_4](^3E_u)$

		Orbital character (%)							
M.o.	*E*/eV	Ru(*s*)	Ru(*p*)	Ru(*d*)	O(*s*)	O(*p*)	C(*s*)	C(*p*)	H(*s*)
$3a_{2u}$	+0.27	19		77		4			
$4e_g$	−9.43			98		2			
$2b_{2g}$	−11.65			88		4		8	
$4a_{1g}$	−12.00	9	1	77		6		4	3
$2b_{1u}$	−12.83			88		12			
$5e_u$	−12.95			29	1	56	2	3	10
$1a_{1u}$	−12.96					100			
$3e_g$	−13.51					100			
$2e_g$	−14.35				2	97		1	
$4e_u$	−14.54		1	64		17	2	7	9
$2b_{2u}$	−14.68			4	3	90		3	
$2a_{2u}$	−14.75	1		3	2	93		2	
$3b_{1g}$	−14.84			17	1	51	3	8	21
$3a_{1g}$	−14.96	2		12	1	53	4	8	19
$1b_{1u}$	−15.30			13		87			
$1a_{2g}$	−17.47					68		32	
$3e_u$	−18.10					68		31	1
$1b_{2g}$	−19.19			12		62		26	
$1e_g$	−19.39		1	1	12	65		21	
$1b_{2u}$	−20.17			16	8	56		20	
$2b_{1g}$	−20.18				14	51	2	29	4
$1a_{2u}$	−20.41	7		5	9	59		20	
$2a_{1g}$	−20.43	1		1	13	50	1	30	4
$2e_u$	−20.59			8	14	50	2	23	4
$1e_u$	−23.58				13	28	25	16	18
$1b_{1g}$	−23.99			8	12	25	27	12	16
$1a_{1g}$	−24.19	4		3	12	27	28	13	14

character of the δ component. Concomitant with this decrease in metal–metal bonding is an increase in metal–oxygen (carboxylate) bonding overlap.

In their theoretical study of dirhodium and diruthenium carboxylates, Norman *et al.*[25] predicted the ground state of $[Ru_2(O_2CH)_4]$ to be ^3E_u with the $^3A_{2g}$ being 2 kcal mol^{-1} higher in energy. The ground state predicted from the *ab initio* calculations reported here shows the opposite trend. There are

Table 5. Valence molecular orbitals from the $\sigma^2\pi^4\delta^2\delta^{*2}\pi^{*4}$ SCF wavefunction for $[Ru_2(O_2CH)_4(NO)_2]$($^1A_{1g}$)

					Carboxylate					Nitrosyl			
M.o.	E/eV	Ru(s)	Ru(p)	Ru(d)	O(s)	O(p)	C(s)	C(p)	H(s)	N(s)	N(p)	O(s)	O(p)
$7e_u$	−0.25			17		1		1			55		26
$5a_{1g}$	−8.91	10	1	68	1	2		3	1	10	2		1
$2b_{1u}$	−10.49			57		43							
$5e_g$	−10.53			60		13		1			10		15
$6e_u$	−11.60			46		30	1		5		6		11
$2b_{2g}$	−12.21			86		6		8					
$1a_{1u}$	−12.21					100							
$4e_g$	−12.83			1		99							
$5e_u$	−13.31			31		41	3	8	13		1		3
$2b_{2u}$	−13.81			3	2	92		2					
$3e_g$	−13.85			12		85		1					
$3b_{1g}$	−13.87			15	1	56	3	6	20				
$3a_{2u}$	−13.88	2		1	2	95		1					
$4a_{1g}$	−14.03	2		4	1	61	5	7	19				
$1b_{1u}$	−15.30			44		56							
$1a_{2g}$	−16.63					68		32					
$4e_u$	−17.28					68		31	1				
$1b_{2g}$	−18.42			14		61		25					
$2e_g$	−18.54		1		12	64		21					
$1b_{2u}$	−19.41			15	9	56		20					
$2b_{1g}$	−19.43			1	12	51	1	29	6				
$3e_u$	−19.64			3	13	50	2	22	5			1	
$2a_{2u}$	−19.71	5		8	9	58		20					5
$3a_{1g}$	−19.74	1		2	11	49	1	30	6				
$1e_g$	−21.64			2		1					40		57
$2e_u$	−21.67			4		1		2	1		38		54
$1a_{2u}$	−22.54	3	1	4						9	33	12	38
$2a_{1g}$	−22.77	1		8						8	31	14	38
$1e_u$	−22.93				14	27	24	15	18		1		1
$1b_{1g}$	−23.29			7	13	24	27	11	17				
$1a_{1g}$	−23.51	4		2	12	26	27	13	14				1

a number of reasons to support our conclusion. First, the experimental geometry as determined from the X-ray crystallographic study of the $[Ru_2(O_2CR)_4(thf)_2]$ complexes shows no Jahn–Teller distortions. This type of geometrical distortion only arises from molecules with degenerate electronic ground states although the size of the distortion may be too small to be detected from the X-ray study. Secondly the *ab initio* theoretical methods used here at the SCF level predict that $^3A_{2g}$ is lower than ^3E_u by 15 kcal mol^{-1}, which is significantly greater than the value of −2 kcal mol^{-1} given by the SW-Xα method. The ^3E_u state has not been studied with the inclusion of the σ/σ^* GVB pair due to limitations of the program for such a large system. The orbital energy splitting (σ–σ^*) is essentially identical for both states, suggesting that the pair energy will be approximately the same for both states. Finally, in terms of orbital eigenvalues the main contribution to the metal–metal bond, the σ orbital, is 0.6 eV lower in the $^3A_{2g}$ than in the ^3E_u state implying a stronger interaction. Our conclusion, that the diruthenium carboxylates should adopt the $\delta^{*2}\pi^{*2}$ rather than the $\pi^{*3}\delta^*$ configuration, has been argued recently from experimental work.[65]

In conclusion, the ground state of $[Ru_2(O_2CH)_4]$ from *ab initio* theoretical calculations is predicted to be $^3A_{2g}$ deriving from a $\sigma^2\pi^4\delta^2\delta^{*2}\pi^{*2}$ metal–metal configuration. The ^3E_u state identified by others[25] as the ground state is predicted to be 15 kcal mol^{-1} higher in energy.

The Ground State of $[Ru_2(O_2CH)_4(NO)_2]$.—The calculated atomic populations for the $^1A_{1g}$ state of $[Ru_2(O_2CH)_4(NO)_2]$, hereafter referred to as (**2**), are given in Table 2 along with the SCF and two-term GVB energies. This state is formally derived from a $\sigma^2\pi^4\delta^2\delta^{*2}\pi^{*4}$ configuration accounting for the observed diamagnetism of the trifluoroacetate derivative.[13] The calculated populations are a little unusual in that they show a total metal π population ($\pi + \pi^*$) of only 6.4 electrons whereas eight are formally required to fill this shell completely, significant interaction with the ligand orbitals accounting for the difference. The total π population is in fact lower than the ^3E_u π population of complex (**1**). This reduced population is due to the effect of the axial nitrosyl ligands (Table 5).

One major difference between the $^3A_{2g}$ state of complex (**1**) and the $^1A_{1g}$ state of complex (**2**) is the character of the π^* orbital, $4e_g$ and $5e_g$, of the two complexes respectively. The former is almost exclusively metal (98%) but the latter is considerably more stable and this is accompanied by an appreciable delocalization onto the nitrosyl (25%) and bridging carboxylate ligands (13%). The metal character in this orbital is reduced to 60% for complex (**2**). In addition to the metal–metal π^* character of this $5e_g$ orbital [complex (**2**)] appreciable metal–nitrosyl bonding character involving the nitrosyl 2π orbital is also present. This stabilization of the metal π^* orbital by the nitrosyl ligand can thus lead to increased interaction between it and the bridging carboxylate ligands. In contrast to the π^* orbital the other metal–metal bonding orbitals except the σ have a little more metal character than the corresponding ones in complex (**1**). The other major difference between the two complexes is the position of the σ orbital [$5a_{1g}$ in complex (**2**)]. This orbital has been considerably raised in the manifold due to a repulsive interaction with the nitrosyl 5σ orbital reflected by its 13% nitrosyl character. The 5σ level in free NO occurs at −18 eV and hence will interact with the $4a_{1g}$ orbital of (**1**) (−12.6 eV) raising the latter. It is interesting that none of the lower a_{1g} or

Table 6. Vertical ionization energies (eV) of $[Ru_2(O_2CCF_3)_4]$ and $[Ru_2(O_2CCF_3)_4(NO)_2]$[33b]

Band	$[Ru_2(O_2CCF_3)_4]$	$[Ru_2(O_2CCF_3)_4(NO)_2]$
a	8.49	8.61
b	9.00	9.57
c	9.66	9.88
d	10.41	10.49

Table 7. Calculated ionization energies (eV) of $[Ru_2(O_2CH)_4]$

State	Ionization energy	Dominant configuration(%)	Assignment of p.e. spectrum
$^4B_{2u}$	9.28	$\sigma^2\pi^4\delta^2\delta^{*1}\pi^{*2}$ (80.8) $\sigma^{*2}\pi^4\delta^2\delta^{*1}\pi^{*2}$ (7.2)	a
^2E_g	10.23	$\sigma^2\pi^4\delta^2\delta^{*2}\pi^{*1}$ (79.4) $\sigma^{*2}\pi^4\delta^2\delta^{*2}\pi^{*1}$ (5.2)	b
$^4B_{1g}$	10.54	$\sigma^2\pi^4\delta^1\delta^{*2}\pi^{*2}$ (72.4) $\sigma^{*2}\pi^4\delta^1\delta^{*2}\pi^{*2}$ (6.7)	c
^4E_u	10.82	$\sigma^2\pi^3\delta^2\delta^{*2}\pi^{*2}$ (87.6) $\sigma^{*2}\pi^3\delta^2\delta^{*2}\pi^{*2}$ (9.3)	d
$^4A_{2g}$	11.44	$\sigma^1\pi^4\delta^2\delta^{*2}\pi^{*2}$ (88.1) $\sigma^{*1}\pi^3\delta^2\delta^{*2}\pi^{*3}$ (8.9)	d

a_{2u} orbitals has any significant ruthenium d character unlike those in complex (**1**). The orbitals with the 5σ nitrosyl character in (**2**) are the $2a_{1g}$ and $1a_{2u}$ at ≈ -22.6 eV. This is appreciably lower than the value for free NO and is presumably due to the significant positive charge on the NO group in this complex.

Assignment of the Experimental P.E. Spectra of $[Ru_2(O_2CCF_3)_4]$ *and* $[Ru_2(O_2CCF_3)_4(NO)_2]$.—The p.e. spectra of the trifluoro derivatives of complexes (**1**) and (**2**) are given in figure 2 of ref. 33(*b*) and the i.e.s are listed in Table 6. The assignment of the p.e. spectra is facilitated by the intensity changes observed when the exciting radiation is changed from He I to He II. Recent studies[66] using synchrotron radiation in studies of the $[Mo_2(O_2CH)_4]$ spectrum show that the ionization intensity of the ($\sigma + \pi$) band decreases by a factor of two when He I is replaced by He II. The intensity of the δ band is unaffected. These results have been used to assign the reported spectra.[33b] We first consider complex (**1**). Bands a and c (Table 6) involve δ and δ^* ionizations with bands b and d involving the σ, π, and π^* ionizations.[33b] The theoretical results given in Table 7 agree well with this assignment. Band a is assigned to the δ^* ionization, b to the π^*, c to the δ, and band d comprises ($\pi + \sigma$) ionizations. The absolute values of the i.e.s are not reproduced well due to the molecule studied theoretically lacking the CF_3 groups present in the experimental work.

Turning now to the p.e. spectrum of the nitrosyl complex, it has been found[33b] that the substitution of He I by He II radiation causes a less dramatic change in band intensity, with the result that no clear assignment of the experimental spectrum can be made.[33b] Our theoretical results, given in Table 8, suggest the following assignment. Band a is assigned to the $\sigma + \delta^*$ since these calculated ionization potentials (i.p.s) have a separation of only 0.3 eV, b/c is ionization from the $\delta + \pi^*$ orbitals, again with a small separation, 0.1 eV, and d assigned to the π ionization. From the experimental data band d does show a small decrease in intensity consistent with it being due to π ionization. Since bands a and b/c both contain a δ/δ^* ionization which will not show an intensity change with He II and an ionization which *will* show a decrease then the drop in intensity of the σ and π^* ionization component may be masked by the δ-type one, especially since the calculated δ^*–σ and δ–π^* separations are so small.

Table 8. Calculated ionization energies (eV) of $[Ru_2(O_2CH)_4(NO)_2]$

State	Ionization energy	Dominant configuration(%)	Assignment of p.e. spectrum
$^2A_{1g}$	7.62	$\sigma^1\pi^4\delta^2\delta^{*2}\pi^{*4}$ (87.1) $\sigma^1\pi^4\delta^2\delta^{*2}\pi^{*3}6e_g{}^1$ (6.1)	a
$^2B_{1u}$	7.91	$\sigma^2\pi^4\delta^2\delta^{*1}\pi^{*4}$ (81.5) $\sigma^{*2}\pi^4\delta^2\delta^{*1}\pi^{*4}$ (6.1)	a
$^2B_{2g}$	8.80	$\sigma^2\pi^4\delta^1\delta^{*2}\pi^{*4}$ (77.6) $\sigma^{*2}\pi^4\delta^1\delta^{*2}\pi^{*4}$ (5.4)	b,c
^2E_g	8.93	$\sigma^2\pi^4\delta^2\delta^{*2}\pi^{*3}$ (83.4) $\sigma^{*2}\pi^4\delta^2\delta^{*2}\pi^{*3}$ (6.3)	b,c
^2E_u	10.00	$\sigma^2\pi^3\delta^2\delta^{*2}\pi^{*4}$ (81.9) $\sigma^{*2}\pi^3\delta^2\delta^{*2}\pi^{*4}$ (5.1)	d

For complex (**1**) the order of decreasing ionization energy by the MRKTSE method is σ, π, δ, π^*, and δ^* with a separation of ≈ 1 eV between the π^* and the δ^* orbitals. However the experimental band intensities do not lead to an unequivocal ordering of the ionic states, nor to a choice between the two possible electronic ground-state configurations. The ordering of ionization energies in complex (**2**) is clearly very different. The most striking difference is the fact that the σ orbital is the lowest-energy ionization. This effect was discussed in relation to the ground-state SCF calculation and is due to repulsion between the closed-shell nitrosyl 5σ orbital and the metal–metal σ-bonding orbital. When compared to the i.e.s given by Koopmans' theorem (Table 5), the values given by the MRKTSE method (Table 8) show two major differences. These are a reduction in the separation of the $^2A_{1g}$ state from the other states arising from metal ionization due to the loss of the σ pair energy in this state, and a change in the ordering of the states due to a greater reduction in the $2b_{2g}$ i.e., which may be attributed to the greater relaxation energy associated with this m.o. which has the largest metal d character.[58]

Conclusion

The calculations on $[Ru_2(O_2CH)_4]$ suggest that the ground state, at the SCF level, is a $\sigma^2\pi^4\delta^2\delta^{*2}\pi^{*2}$ configuration with the $\sigma^2\pi^4\delta^2\pi^{*3}\delta^*$ configuration 15 kcal mol^{-1} higher in energy. This former configuration has been argued for in recent work by Cotton and Matusz[65] as well as being consistent with work on $[Mo_2(O_2CH)_4]$[34] and $[Rh_2(O_2CH)_4(H_2O)_2]^+$.[38] The p.e. spectrum is assigned consistently on the basis of MRKTSE calculations assuming such a ground state. There is the possibility that this complex has a $\sigma^2\pi^4\delta^2\pi^{*3}\delta^*$ degenerate electronic ground state (^3E_u) and Jahn–Teller distortions sufficient to lower the energy below the $^3A_{2g}$ energy. Optimization of the geometry of a complex of this size, in an all-electron basis, is beyond our capabilities at present.

The calculation on the diamagnetic species $[Ru_2(O_2CH)_4(NO)_2]$ clearly shows a formal $\sigma^2\pi^4\delta^2\delta^{*2}\pi^{*4}$ configuration. The SCF results and the calculated i.e.s show that the σ orbital is raised to be the highest occupied molecular orbital in the SCF level calculation and also corresponds to the lowest-energy i.e. The π^* level has also been stabilized, by interaction with the 2π orbitals on the nitrosyl ligand. The MRKTSE calculations of the i.e.s of this complex clearly show the need for including both correlation and relaxation effects in a description of the ionic states.

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