Applications of Magnetic Circular Dichroism Spectroscopy: Excited States of Oxocarbon Dianions

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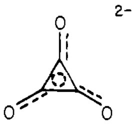
Abstract: UV-visible absorption and magnetic circular dichroism of the $C_4O_4^{2-}$, $C_5O_5^{2-}$, and $C_6O_6^{2-}$ dianions have been measured and analyzed qualitatively in terms of the perimeter model and quantitatively by π-electron and all-valence-electron calculations. The results provide an understanding of low-energy ππ* states. They further suggest that many "nπ*" states are present at relatively low energies.

Introduction

The cyclic oxocarbon dianions **1-4** constitute a homologous series of highly symmetrical species, often described as aromatic.[2] Croconate (**3**) and rhodizonate (**4**) ions have been known since early in the 19th century, and the long-wavelength absorption bands of these species and of squarate ion (**2**) have been mentioned repeatedly in the literature[2] and frequently used in spectrophotometric determinations of acid strength for these species.[3]



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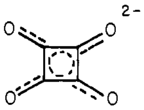

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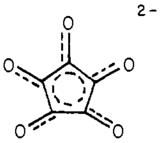

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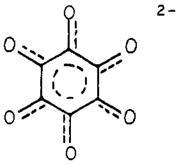

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The dominant feature in the electronic spectrum of each of the oxocarbon anions is an intense band which must represent the first allowed $\pi \rightarrow \pi^*$ transition. As was pointed out some years ago, this band has the same shape for each of the three species, with a strong shoulder on the high-frequency side[2b] (Figure 1). In a series of elegant resonance-Raman spectroscopic studies, Ito and his students[4] have shown that this doubling is due to Jahn-Teller distortion in the excited ππ* state, which is required by symmetry to be doubly degenerate for all of the oxocarbon dianions.

In view of the interest in the oxocarbons and their electronic structure over the past 15 years, it is remarkable that no complete electronic spectra appear to be published for any of these species. In this paper we report the electronic absorption and magnetic circular dichroism of **2**, **3**, and **4**, and analyze them in terms of a simple MO model and of semiempirical all-valence-electron calculations. We confirm the validity of the recent prediction[5] of the absolute MCD signs of the first ππ* transitions based on the perimeter model, in which the oxocarbon dianions were viewed as perturbed two-electron [*n*]annulenes.

Experimental Section

Dipotassium rhodizonate (Aldrich Chemical Co.) was purified by rapid recrystallization from deoxygenated water. Dipotassium croconate was obtained from the rhodizonate by air oxidation in aqueous solution following the time-honored method originally described by Nietzki and Benckiser,[6] and was recrystallized from water. Disodium squarate was synthesized as described earlier[7] and recrystallized from water. These oxocarbon salts all gave satisfactory analyses for carbon.

The electronic spectra were determined on aqueous solutions using a Cary Model 17 spectrometer. For rhodizonate deoxygenated water was used, and transfers and dilutions were effected under nitrogen. Oscillator strengths were obtained from $f = 4.319 \times 10^{-9} \int \epsilon \, d\bar{\nu}$, dipole strengths from $D = 9.1834 \times 10^{-3} \int d\bar{\nu} \epsilon / \bar{\nu}$. The MCD spectra were first determined using a Cary Model 60 dichrograph equipped with a 45-kG superconducting magnet as described in ref 8, and later redetermined using a JASCO 500C spectropolarimeter with a 15-kG electromagnet as described in ref 9, with results in excellent agreement. The values of A terms were obtained from the relation $A = 33.53^{-1} \int d\bar{\nu} (\bar{\nu} - \bar{\nu}_0)[\theta]_M / \bar{\nu}$, where $\bar{\nu}$ is wavenumber, $\bar{\nu}_0$ is the band center, and $[\theta]_M$ is molar ellipticity per unit magnetic field in units of deg L m^{-1} mol^{-1} G^{-1}, and magnetic moments of excited states μ were obtained from the relation $\mu = -2A/D$.

Molecular orbital calculations were performed by the INDO/S method[10] using an SCF-CI program provided by Professor Michael Zerner (University of Guelph) to obtain wave functions. These were used to calculate transition moments and MCD A and B terms using the sum-over-states formula, similarly as in ref 11. Matrix elements of the requisite operators over AO's were evaluated exactly for Slater type AO's. Formulas for dipole velocity[12] and magnetic moment[13] were programmed, and a subroutine for the dipole length operator was obtained from Professor Frank Harris (University of Utah). The transformation of the matrix elements from AO to MO basis was done after Löwdin deorthogonalization of the INDO/S molecular orbitals (cf. ref 11).

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(1) (a) University of Utah; (b) University of Wisconsin; (c) presented in part at the Oxocarbon Symposium, ACS Annual Meeting, Sept 9-14, 1979, Washington, D.C. The proceedings of the symposium have appeared in a book form: "Oxocarbons", R. West, Ed., Academic Press, New York, 1980.

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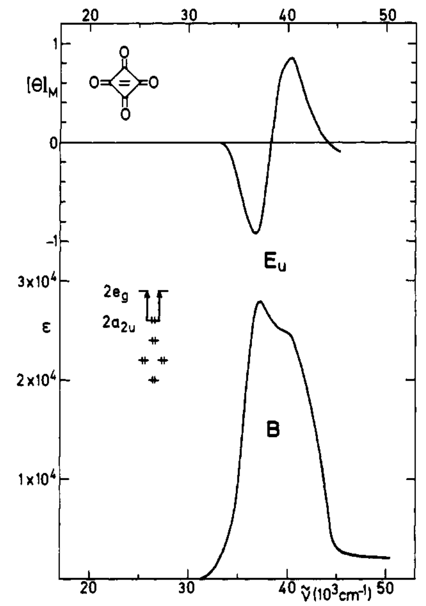

Figure 1. Sodium squarate. Top, MCD spectrum; bottom, absorption spectrum (in water). The observed transition is of type B. Excited-state symmetry and a schematic representation of the dominant configuration are also shown. The D_{4h} symmetry labels of initial and final MO's are given; the correspondence to the C_4 group labels used in the text is $a_{2u} \rightarrow \epsilon_0$; $e_g \rightarrow \epsilon_1, \epsilon_{-1}$; $b_{1u} \rightarrow \epsilon_2 \equiv \epsilon_{-2}$.

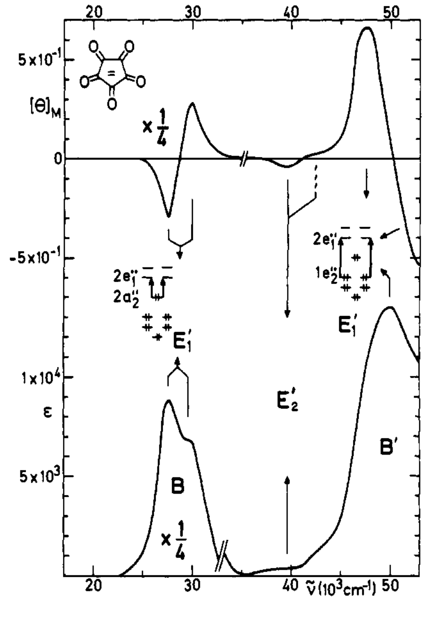

Figure 2. Potassium croconate. Top, MCD spectrum; bottom, absorption spectrum (in water). The assignment of the allowed transitions B and B' is shown. Center, excited state symmetry and schematic representation of the dominant configuration. Allowed electron transitions are shown as full lines. The D_{5h} symmetry labels of initial and final MO's are shown. They correspond to the C_5 group lables used in the text as follows: $a_2'' \rightarrow \epsilon_0$; $e'' \rightarrow \epsilon_1, \epsilon_{-1}$; $e'' \rightarrow \epsilon_2, \epsilon_{-2}$.

Similar results for the $\pi\pi^*$ states were obtained using the standard PPP procedure outlined in ref 14. The high symmetry of the oxocarbon dianions guarantees origin independence of the MCD results.

Results

The absorption and MCD spectra of the dianions **2–4** are shown in Figures 1-3. The assignment of individual transitions shown in the figures is based on the comparison of the shapes of the absorption and MCD spectra. The latter make it quite clear that all observed transitions involve doubly degenerate excited states. The upper-state symmetry labels shown were assigned on the basis of the observed intensity, assuming $\pi\pi^*$ excitations, since $n\pi^*$ transitions are usually very weak both in absorption and MCD. They agree with the theoretical analysis. The labels B and B' represent a generalization of the Platt nomenclature[15] for excited states of aromatic π systems, as discussed in more detail below. In our view, the number of transitions assigned is the minimum necessary to account for all observed features in the spectra. However, it is quite possible that additional unobserved weak transitions are present. Such transitions might be responsible for the long-wavelength tail of the first absorption band assigned as transition B. Indeed, in ref 16 weak absorption at 31 000 cm^{-1} in C_4O_4 (ϵ = 174) was assigned as a $n\pi^*$ transition. It seems to us, however, that further experimental evidence will be needed for definitive assignment of $n\pi^*$ transitions in the spectra of the dianions **2–4**.

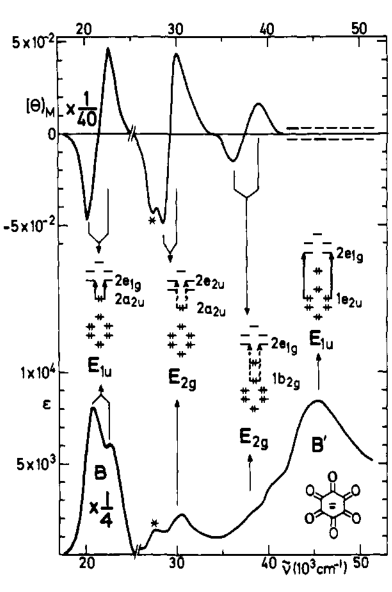

Figure 3. Sodium rhodizonate. Top, MCD spectrum; bottom, absorption spectrum (in water). The asterisks mark peaks due to a $C_5O_5^{2-}$ impurity. The dashed lines indicate the maximum MCD signal level for the B' transition. The assignment of the allowed transitions B and B' is shown. Center, excited state symmetry and schematic representation of the dominant configuration. Allowed electron transitions are shown as full lines, forbidden ones as dashed lines. The D_{6h} symmetry labels of initial and final MO's are shown. They correspond to the C_6 group labels used in the text as follows: $a_{2u} \rightarrow \epsilon_3$; $e_{1g} \rightarrow \epsilon_1$; $e_{21} \rightarrow \epsilon_2, \epsilon_{-2}$; $B_{2g} \rightarrow \epsilon_3 \equiv \epsilon_{-3}$.

Table I summarizes the experimental transition energies, oscillator strengths, and excited state magnetic moments, and compares them with the calculated values. Magnetic moments are in units of Bohr magneton (β_e) and B terms in units of $10^{-3}\beta_e$ D^2 cm^{-1}. States indicated as $n\pi^*$ are excitations from the highest occupied "nonbonding" orbital to the lowest free π^* orbital. For $\pi\pi^*$ states, the dominant configurations are indicated.

Discussion

Molecular Orbitals of the Oxocarbon Dianions $C_nO_n^{2-}$. In order to derive a qualitative MO scheme for the $C_nO_n^{2-}$ skeleton, we consider it as originating from CO units interacting through their carbon termini. As shown on the right-hand side of Figure 4, each of these contributes a strongly bonding π_{CO} orbital, and a strongly antibonding π^*_{CO} orbital. If we consider only the first-order interactions between degenerate orbitals, the n low-energy π_{CO} orbitals will interact to produce a set C–O bonding delocalized orbitals of the $C_nO_n^{2-}$ skeleton, to which we shall refer as group 1. The n π^*_{CO} orbitals will similarly produce a set of n C–O antibonding delocalized orbitals, to which we shall refer as group 2. Within each group the most stable orbital will be of symmetry $\epsilon_0 \equiv a$ followed by a degenerate pair of symmetry ϵ_1, ϵ_{-1}, etc., and eventually by the least stable orbital of the group, either the $\epsilon_{(n/2-1},$

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Table I. Electronic States of Oxocarbon Dianions

	E, 10^3 cm^{-1}		f		MCD				
species	exptl	calcd	exptl	calcd	μ_{exptl}	μ_{calcd}	B	symmetry	dominant configurations
$C_3O_3{}^{2-}$		32.8		0		0	0	A_1''	
		36.0		0.22		−0.16	0	E'	$2\epsilon_0 \rightarrow 2\epsilon_1, 2\epsilon_{-1}$
		37.3		0		0	0	E''	
		44.8		0.02		0	0.44	A_2''	$n\pi^*$
		47.9		0		0	0	E''	
		55.2		0		0	0	A_1''	
$C_4O_4{}^{2-}$		24.1		0		0	0	E_g	
	39.0	29.2	0.9	0.48	−0.30	−0.22	0	E_u	$2\epsilon_0 \rightarrow 2\epsilon_1, 2\epsilon_{-1}$
		30.7		0		0	0	A_{1u}	
		33.5		0		0	0	B_{2u}	
		39.1		0		0	0	B_{2u}	
		43.3		0		0	0	B_{2g}	$2\epsilon_0 \rightarrow 2\epsilon_2$
		43.3		0.02		0	0.79	A_{2u}	$n\pi^*$
		43.5		0		0	0	B_{2u}	
		47.6		0		0	0	E_g	
		50.3		0		0	0	A_{2g}	
$C_5O_5{}^{2-}$		19.7		0		0	0	E_1''	
		20.3		0		0	0	E_2''	
	28.5	21.7	0.7	0.50	−0.25	−0.22	0	E_1'	$2\epsilon_0 \rightarrow 2\epsilon_1, 2\epsilon_{-1}$
		28.1		0		0	0	A_1''	
		38.4		0		0	0	E_2''	
		38.9		0		0	0	E_1''	
	41.0	39.7		0		0	0	E_2'	$2\epsilon_0 \rightarrow 2\epsilon_{+2}, 2\epsilon_{-2}$
		40.5		0		0	0	E_2''	
		42.5		0.01		0	0.97	A_2''	$n\pi^*$
	(41.0)	50.1		0		0	0	E_2'	$1\epsilon_2 \rightarrow 2\epsilon_{-1}, 1\epsilon_{-2} \rightarrow 2\epsilon_1$
		50.7		0		0	0	A_1''	
	50.0	51.7	0.4	0.53	>0	+0	0	E_1'	$1\epsilon_2 \rightarrow 2\epsilon_1, 1\epsilon_{-2} \rightarrow 2\epsilon_{-1}$
$C_6O_6{}^{2-}$		15.1		0		0	0	E_{2u}	
	21.5	16.5	0.5	0.52	−0.35	−0.21	0	E_{1u}	$2\epsilon_0 \rightarrow 2\epsilon_1, 2\epsilon_{-1}$
		21.8		0		0	0	E_{1g}	
		22.3		0		0	0	B_{1g}	
		27.0		0		0	0	A_{1u}	
		30.5		0		0	0	B_{2g}	
	30.0	30.6		0		0	0	E_{2g}	$2\epsilon_0 \rightarrow 2\epsilon_2, 2\epsilon_{-2}$
		32.7		0		0	0	B_{2g}	
		37.2		0		0	0	E_{2u}	
		37.5		0		0	0	E_{1g}	
		39.2		0		0	0	B_{1u}	$2\epsilon_0 \rightarrow 2\epsilon_3$
		40.1		0		0	0	E_{2u}	
		42.9		0.01		0	0.70	A_{2u}	$n\pi^*$
		44.7		0		0	0	E_{1g}	
		47.9		0		0	0	A_{2g}	
		48.9		0		0	0	A_{1u}	
	38.0	51.0		0		0	0	E_{2g}	$1\epsilon_3 \equiv 1\epsilon_{-3} \rightarrow 2\epsilon_1, 2\epsilon_{-1}$
		52.1		0		0	0	B_{2u}	$1\epsilon_2 \rightarrow 2\epsilon_{-1}, 1\epsilon_{-2} \rightarrow 2\epsilon_{;1}$
		53.1		0		0	0	E_{2u}	
	45.5	55.3	~0.4	0.32	$\lvert\mu\rvert < 0.005$	−0.03	0	E_{1u}	$1\epsilon_2 \rightarrow 2\epsilon_1, 1\epsilon_{-2}, 2\epsilon_{-1}$

$\epsilon_{-(n/2-1)}$ pair, if n is odd, or the $\epsilon_{n/2} \equiv \epsilon_{-n/2} \equiv b$ orbital, if n is even. Next, second-order mixing between the resulting bonding and antibonding groups of orbitals is allowed to occur. This step does not change the overall picture, but permits the degree of C–O bonding or antibonding to vary from one MO to another. Still, the orbitals of group 1 will generally remain C–O bonding, and those of the higher energy group 2, generally C–O antibonding. Within each group, the lowest orbital (a) will be purely C–C bonding, and the highest, strongly C–C antibonding, with a gradual transition from one extreme to the other. The resulting MO scheme is closely related to that of a simple annulene perimeter discussed, e.g., in ref 5, except that it is doubled and occurs once for bonding orbitals of group 1 and once for antibonding orbitals of group 2.

Although the above derivation of the MO scheme for the oxocarbon dianions is simple and instructive, it does not allow easy estimates of the magnitude of the magnetic moments associated with the various orbitals. In order to obtain these, we now rederive the scheme in an alternative manner, shown on the left-hand side of Figure 4. Here, we first construct the ordinary perimeter orbitals from the carbon AO's and label them $\epsilon_0(C)$, $\epsilon_1(C)$, $\epsilon_{-1}(C)$, etc. Then we combine the $2p_z$ orbitals on the oxygens into symmetry orbitals, $\epsilon_0(O)$, $\epsilon_1(O)$, $\epsilon_{-1}(O)$, etc. Since the O–O resonance integrals are negligible because of the large O–O separation between even the nearest oxygen atoms, these symmetry orbitals will all be of about the same energy and will remain nonbonding. Moreover, they will have negligible magnetic moments.

Now, the carbon perimeter orbitals, $\epsilon_k(C)$, and the oxygen symmetry orbitals, $\epsilon_k(O)$, are allowed to interact. Orbitals of like symmetry will act as if their energies repelled, and the degree of the effect will be dominated by their separation of the energy scale. The lower energy combination, $\epsilon_k(C) + \epsilon_k(O)$, will be identical with one of the MO's of the previously discussed group 1. It will be bonding along the C–O bonds corresponding to the new interactions and will consist primarily of that original orbital $\epsilon_k(C)$ or $\epsilon_k(O)$ which was lower in energy. The higher energy combination, $\epsilon_k(C)-\epsilon_k(O)$, will correspond to one of the MO's of the previously discussed group 2. It will be C–O antibonding and will consist predominantly of that original orbital which was of higher energy. The numerical calculations suggest that the energy of the nonbonding oxygen orbitals is comparable to that of the ϵ_1, ϵ_{-1} bonding pair of the carbon perimeter orbitals, so that they will mix in a roughly one-to-one ratio. The oxygen orbitals are of relatively lower energy in very small rings where the ϵ_1, ϵ_1 pair is nonbonding ($n = 4$) or even antibonding ($n = 3$). In general however, the $\epsilon_{\pm1}(C)-\epsilon_{\pm1}(O)$ mixing is stronger than any other and

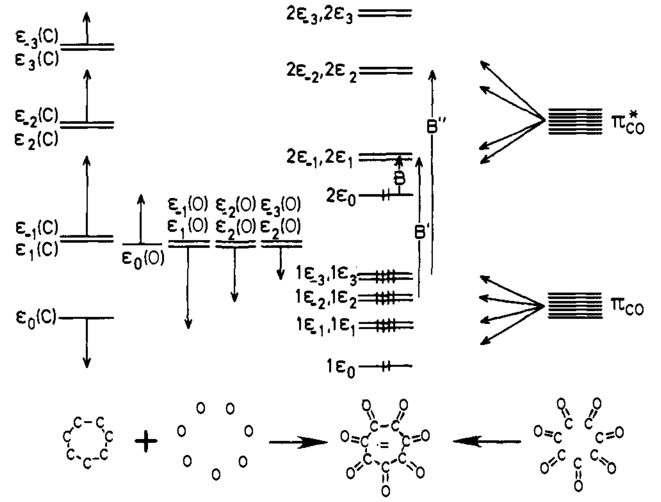

Figure 4. On the left, qualitative derivation of the MO's of a $C_nO_n^{2-}$ dianion ($n = 7$) from those of the perimeter orbitals $\epsilon_k(C)$ and the oxygen symmetry orbitals $\epsilon_k(O)$. On the right, their relation to those of the bonding (π_{CO}) and antibonding (π_{CO}*) bond orbitals of the constituent carbonyl groups. The first three allowed transitions, B, B′, and B″, are indicated.

produces two widely split ϵ_1, ϵ_{-1} pairs of MO's: $1\epsilon_{\pm1}$ and $2\epsilon_{\pm1}$. The ϵ_0 symmetry orbital of the oxygens, $\epsilon_0(O)$, is pushed up in energy by interaction with $\epsilon_0(C)$ which is lower but close enough for a reasonably effective mixing. Both all-valence-electron and π-electron calculations suggest that the weight of $\epsilon_0(C)$ in the lower of the two resulting MO's, $1\epsilon_0$, is somewhere between two-thirds and three-quarters of the total, while its weight in the upper of the resulting MO's, $2\epsilon_0$, is between a quarter and a third. The remaining symmetry orbitals on the oxygens, $\epsilon_{\pm2}(O)$, $\epsilon_{\pm3}(O)$, etc., are all pushed down in energy by interaction with the higher carbon perimeter orbitals, $\epsilon_{\pm2}(C)$, $\epsilon_{\pm3}(C)$, etc., in progressively smaller amounts as the energy separation $\epsilon_{\pm k}(O)-\epsilon_{\pm k}(C)$ increases with increasing k. At the same time, the resulting bonding orbitals $1\epsilon_{\pm2}$, $1\epsilon_{\pm3}$, etc., become more purely localized on oxygen atoms alone. The calculations suggest that the weight of $\epsilon_{\pm2}(C)$ in $1\epsilon_{\pm2}$ is only about one-fifth and that the weight of the $\epsilon_{\pm k}(C)$ decreases further for higher $1\epsilon_{\pm k}$'s.

These results are in qualitative agreement with those of esr measurements on the related radical anions.[17] In the ground state of the dianions $C_nO_n^{2-}$, all orbitals of group 1 and the most stable among the orbitals of group 2, $2\epsilon_0$, are occupied by the $2n + 2$ π electrons present. The g value for $C_6O_6^{3-}$ (unpaired electron in $2\epsilon_{\pm1}$) is lower than that for $C_6O_6^-$ (unpaired electron in $2\epsilon_0$), as expected if the weight of $\epsilon_{\pm1}(C)$ in $2\epsilon_{\pm1}$ is larger than the weight of $\epsilon_0(C)$ in $2\epsilon_0$. The ^{13}C coupling constant in $C_5O_5^-$ (unpaired electron in $2\epsilon_0$) suggests that $\epsilon_0(O)$ dominates over $\epsilon_0(C)$ in $2\epsilon_0$. Because contribution of the $\epsilon_{\pm k}(O)$ orbitals to the magnetic moments of the resulting MO's is virtually zero, we can estimate the relative magnitude of the magnetic moments of the final MO's from the knowledge of the relative weights of $\epsilon_{\pm k}(C)$ and $\epsilon_{\pm k}(O)$ in $1\epsilon_{\pm k}$ and $2\epsilon_{\pm k}$ and the knowledge[5] of the magnetic moments of an electron in $\epsilon_{\pm k}(C)$. In the case of n = 5 to 7, the magnetic moments of the orbitals $\epsilon_{\pm1}(C)$ and $\epsilon_{\pm2}(C)$ do not differ much, so that the relative weight of $\epsilon_{\pm k}(C)$ and $\epsilon_{\pm k}(O)$ alone permits an estimate to be made; the magnetic moments of MO's $1\epsilon_{\pm1}$ and $2\epsilon_{\pm1}$ should be comparable and quite large while those of the higher orbitals of group 2 will be large only until one gets near the upper end of the MO spectrum, and those of the higher orbitals of group 1 will always be small.

Electronic States of the Oxocarbon Dianions $C_nO_n^{2-}$. In the following, we shall approximate singlet states by single configurations. It is known that the mixing of the ground configuration with doubly excited configurations needs to be considered if the singlet–triplet splitting is to be understood,[18] but this will not concern us here. This simplification is justified by the results of our all-valence-electron and π-electron calculations, in which configuration mixing is included but is found to be of secondary importance.

The MO scheme of Figure 4 suggests that, in addition to the $2\epsilon_0 \rightarrow 2\epsilon_{\pm1}$ configuration obtained by promoting an electron from the highest occupied MO (HOMO) to the lowest unoccupied MO (LUMO), there will be a large number of other excited singlet configurations at relatively low energies. These correspond to excitations from $2\epsilon_0$ or the various occupied orbitals of group 1 into the LUMO pair ($2\epsilon_{\pm1}$), into the next higher vacant orbital pair ($2\epsilon_{\pm2}$), etc. Relatively few of these configurations will be of E_1 symmetry, which is required if transitions into them are to be symmetry allowed. These will be the configuration pairs of the type $\epsilon_k \rightarrow \epsilon_{k\pm1}$, $\epsilon_{-k} \rightarrow \epsilon_{-(k\pm1)}$.[5] The electron promotion $1\epsilon_{(n-1)/2} \rightarrow 2\epsilon_{(n-1)/2}$ for n odd will also produce an allowed transition into a configuration of symmetry E_1', but this is likely to lie at higher energy and will be of little interest in the present context. The most important among the excited singlet excitations of the allowed type is the one which produces the lowest energy excited configuration, $2\epsilon_0 \rightarrow 2\epsilon_{\pm1}$. This excitation is completely analogous to the $\epsilon_0 \rightarrow \epsilon_{\pm1}$ excitation in a simple two-electron annulenylium cation, such as the hypothetical cyclobutadiene dication $C_4H_4^{2+}$, and it was on this basis that the prediction of positive A terms for this transition in the oxocarbon dianions was made in ref 5. Among configurations obtained by transitions from orbitals of group 1 into the LUMO pair $2\epsilon_{\pm1}$, two are configuration pairs of the allowed E_1 symmetry. One of these pairs, $1\epsilon_0 \cdot 2\epsilon_{\pm1}$, must be at very high energies, while the other pair, $1\epsilon_2 \rightarrow 2\epsilon_1$ and $1\epsilon_{-2} \rightarrow 2\epsilon_{-1}$, is more likely to be observed. The latter pair of configurations has no analogy in the simple $(4N + 2)$-electron $[n]$-annulenes discussed in ref 5, in which the order of MO's is such that if $\epsilon_{\pm k}$ is vacant in the ground configuration, all $\epsilon_{\pm j}$ pairs for which $j > k$ are higher in energy and therefore also vacant in the ground configuration. Proceeding to consider promotions into the orbital pair $2\epsilon_{\pm2}$, we note that the allowed transitions will originate in $1\epsilon_{\pm1}$ and $1\epsilon_{\pm3}$ (if $n = 6$, $1\epsilon_3 \equiv \epsilon_{-3} \equiv \beta$, and if $n < 6$, $\epsilon_{\pm3}$ does not exist), but these are likely to be at high energies and difficult to observe for small values of n.

In addition to these allowed transitions, a large number of forbidden transitions should be present. These will be of two types: some will originate in electron promotions from the higher orbitals of group 1 into the $2\epsilon_{\pm1}$ pair and, at higher energies, into the $2\epsilon_{\pm2}$ pair, etc. Others will be analogous to Platt's L transitions in simple $(4N + 2)$ annulenes,[13] in that they will be sense-reversing excitations between a pair of degenerate orbitals which also produced an allowed transition: $\epsilon_k \rightarrow \epsilon_{-(k+1)}$, $\epsilon_{-k} \rightarrow \epsilon_{k+1}$. The upper states will be degenerate, of symmetry E_{2k+1}. If n is even, the E_{2k+1} representation may not exist and the upper states will then be nondegenerate and of symmetry A or B.

In summary then, the spectrum should commence with an allowed transition $2\epsilon_0$ $2\epsilon_{u1}$ of E_1 symmetry, analogous to the B transition in two-electron annulenylium ions. Because of this analogy, we propose the label B transition for this characteristic first $\pi\pi$* transition of the $C_nO_n^{2-}$ oxocarbon dianions. For $n > 3$, the next allowed transition into an E_1 state should correspond to the pair of excitations of type B, $1\epsilon_2 \rightarrow 2\epsilon_1$ and $1\epsilon_{-2} \rightarrow 2\epsilon_{-1}$, and we propose to label it B′. If $n = 4$, $\epsilon_2 \equiv \epsilon_{-2}$, so that the corresponding forbidden transition pair of the L type, $1\epsilon_2 \rightarrow 2\epsilon_{-1}$ and $1\epsilon_{-2} \rightarrow 2\epsilon_1$, will be missing. If $n \geq 6$, the allowed absorption due to another pair of excitations of type B, $1\epsilon_3 \rightarrow 2\epsilon_2$ and $1\epsilon_{-3} \rightarrow 2\epsilon_{-2}$, which we shall refer to as B″, will appear at even higher energies, etc. In addition to these allowed $\pi\pi$* transitions, the spectrum might contain features due to forbidden $\pi\pi$* transitions with intensity provided by vibronic interactions, and possibly also some due to nπ* transitions which we have been ignoring so far.

As n increases, a larger number of orbitals will be available, and a larger number of both allowed and forbidden transitions will be possible. In particular, an increasing number of sym-

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(17) E. Patton and R. West, *J. Phys. Chem.*, **77**, 2652 (1973).

(18) K. Sakamoto and Y. J. I'Haya, *J. Am. Chem. Soc.*, **92**, 2636 (1970), and references therein.

metry-forbidden $\pi\pi^*$ transitions will occur in the experimentally interesting region between the B and B′ transitions. The results of calculations presented in Table I and those in ref 18 suggest that in $C_4O_4^{2-}$ this region will contain none, in $C_5O_5^{2-}$, one or two (E'_2: $1\epsilon_2 \rightarrow 2\epsilon_{-1}$, $1\epsilon_{-2} \rightarrow 2\epsilon_1$, and $2\epsilon_0 \rightarrow 2\epsilon_{\pm2}$), in $C_6O_6^{2-}$, three or four ($2 \times E_{2g}$ from $1b \rightarrow 2\epsilon_{\pm1}$ and $2a \rightarrow 2\epsilon_{\pm2}$; B_{1u} and B_{2u} from the pair $1\epsilon_2 \rightarrow 2\epsilon_{-1}$, $1\epsilon_{-2} \rightarrow 2\epsilon_1$). Further, even if it is assumed that the C–O and C–C bond lengths and resonance integrals remain constant, the excitation energies of transitions of the various types should decrease with increasing *n*, just as they do in the simple $(4N + 2)$-electron [*n*]annulenes.

At this point we can compare our deductions with the absorption spectra shown in Figures 1–3. Spectral patterns observed are exactly those anticipated. There are two intense absorption bands, decreasing in energy with increasing *n* in $C_nO_n^{2-}$, which we accordingly assign as due to the B transition and the B′ transition in the order of increasing energy. In $C_4O_4^{2-}$, the B′ transition is out of the range of our instrumentation. In the spectra of $C_5O_5^{2-}$ and $C_6O_6^{2-}$, indications of additional very weak transitions are observed in the region between the B and B′ bands. These are probably the expected forbidden $\pi\pi^*$ transitions, but detailed assignment is difficult on the basis of absorption alone.

A more definitive confirmation of the validity of the theoretical analysis can be obtained from the MCD spectra. From a previous discussion of the origin of the MCD signs in simple $(4N + 2)$-electron [*n*]annulenes[5] it is clear that the degenerate pair of excitations $\epsilon_k \rightarrow \epsilon_{k+1}$, $\epsilon_{-k} \rightarrow \epsilon_{-(k+1)}$ produce a positive *A* term if the magnetic moment of an electron in orbital ϵ_{k+1} is larger in absolute value than that of an electron in orbital ϵ_k, and a negative *A* term if it is smaller.

Unlike simple annulenes, the $C_nO_n^{2-}$ dianions also permit excitations of the type $\epsilon_{k+1} \rightarrow \epsilon_k$, $\epsilon_{-(k+1)} \rightarrow \epsilon_{-k}$ and they need to be considered as well. Arguments similar to those described in ref 5 show that if the magnetic moment of the orbitals ϵ_k is less negative than that of ϵ_{k+1}, this excitation will have a positive *A* term. If the magnetic moment of ϵ_k is more negative than that of ϵ_{k+1}, a negative *A* term will result. In summary then, the sign of the *A* term of the pair of electron transitions between ϵ_k and ϵ_{k+1} and between ϵ_{-k} and $\epsilon_{-(k+1)}$ does not depend on whether the excitation is from *k* to $k + 1$ or from $k + 1$ to *k*. In either case, the *A* term will be positive if the absolute value of the magnetic moment of an electron in the orbital pair $\epsilon_{\pm(k+1)}$ is larger than that of an electron in the orbital pair $\epsilon_{\pm k}$, and negative if the opposite is true.

We are new ready to make qualitative predictions of MCD signs for the allowed transitions B and B′. Since the orbital $2\epsilon_0$ has no magnetic moment, while the orbitals $2\epsilon_{\pm1}$ do, there is no doubt about the sign of the *A* term of the B transition, represented by the $2\epsilon_0 \rightarrow 2\epsilon_{\pm1}$ pair of excitations: it must be positive. The next allowed transition, B′, corresponds to the pair of excitations $1\epsilon_2 \rightarrow 2\epsilon_1$, $1\epsilon_{-2} \rightarrow 2\epsilon_{-1}$. This transition does not exist in $C_3O_3^{2-}$. In $C_4O_4^{2-}$, $1\epsilon_2 \equiv 1\epsilon_{-2} \equiv b$. This nondegenerate orbital has a zero magnetic moment, while the orbitals of the pair $2\epsilon_{\pm1}$ have a nonzero moment, so that the sign of the *A* term of the B′ transition is negative. In $C_5O_5^{2-}$ and higher members of the series, both the starting ($1\epsilon_{\pm2}$) and ending ($2\epsilon_{\pm1}$) orbitals involved in the B′ transition are degenerate and have nonvanishing magnetic moments. It now becomes essential to know the relative magnitudes of the magnetic moments of the various orbitals. Our analysis suggested strongly that the orbital pair $2\epsilon_{\pm1}$ has a large magnetic moment, since it contains a heavy contribution from the carbon perimeter orbital pair $\epsilon_{\pm1}$(C). On the other hand, the orbital pair $1\epsilon_{\pm2}$ should have a smaller magnetic moment, since it is primarily composed of the oxygen symmetry orbital pair $\epsilon_{\pm2}$(O). There is little doubt that the conclusion is correct for $n = 5$, but for higher *n* it will be on somewhat shakier ground, both because of the increasing content of $\epsilon_{\pm2}$(C) in the orbital pair $1\epsilon_{\pm2}$ (Figure 4), and because the magnetic moment of $\epsilon_{\pm2}$(C) gradually becomes substantially larger than that of $\epsilon_{\pm1}$(C) as *n* increases, while they were comparable for $n = 5$ to 7. At least for the lower members of the homologous series, however, we predict a negative *A* term for the B′ transition. It is possible to carry the analysis further. For instance, for $n \geq 6$, another allowed transition, B″, appears at higher energies, and its *A* term should be negative. However, there is little point in continuing the analysis at present, since the larger members of the homologous series in which these higher allowed transitions might be observable are not known.

The neglect of vibronic interactions throughout our qualitative discussion makes it impossible to predict the signs of the MCD effects of forbidden transitions, which acquire intensity only by vibronic coupling. It also makes it impossible to discuss the Jahn–Teller distortions possibly present in the degenerate excited states. The observed MCD spectra are certainly compatible with the resonance Raman evidence for Jahn–Teller distortions in the B excited state of the ions $C_4O_4^{2-}$, $C_5O_5^{2-}$, and $C_6O_6^{2-}$, in that the two peaks observed for the transition in absorption spectra correspond jointly to a single s-shaped MCD curve rather than separately to one s-shaped MCD curve each. The existence of the Jahn–Teller distortion does not affect our arguments concerning the sequence of absolute signs in the MCD spectra.

A comparison with the MCD curves of Figures 1–3 confirms the assignment of the B and B′ transitions which are noted to have positive and negative *A* terms, respectively, where these can be observed. It is now also possible to analyze further the nature of the weak additional transitions between the B and B′ bands. In $C_5O_5^{2-}$ a weak positive *A* term is observed in this region, partially obscured by overlap with the B′ band. This shows that the upper state of the forbidden transition is degenerate and leads us to assign it as one of the forbidden $\pi\pi^*$ transitions of symmetry E_2' predicted by theory for this region. In $C_6O_6^{2-}$ two positive *A* terms are present in the region between the B and B′ transitions, corresponding to two transitions with degenerate upper states. Theory predicts two degenerate states of E_{2g} symmetry, to which we assign the observed *A* terms, and two forbidden transitions into states of B_{2u} and B_{1u} symmetry, for which we detect no experimental evidence at present.

The agreement between the qualtiative analysis for $\pi\pi^*$ transitions and the observed absorption and MCD spectra is excellent. The quantitative calculations for these transitions by the π electron and all-valence-electron methods mostly agree very well with each other and with the qualitative arguments, including magnetic moment signs and magnitudes (Table I). The differ in the assignment of the electron transitions involved in the two E'_2 transitions in $C_5O_5^{2-}$ and both possibilities are indicated in Table I. They suggest also that the $C_6O_6^{2-}$ considerable mixing of the configurations responsible for the two E_{2g} states occurs ($2a_0 \rightarrow 2\epsilon_{\pm2}$ and $1b \rightarrow 2\epsilon_{\pm1}$). Interestingly, the INDO/S results shown in Table I yield an almost vanishing value for the magnetic moment of the B′ state of $C_6O_6^{2-}$, and all our efforts to measure the MCD of the transition into this state yielded only noise, indicating that its *A* term and the magnetic moment are very small indeed (the qualitative analysis predicts a positive magnetic moment but says little about its magnitude). The relative calculated excitation energies for different $\pi\pi^*$ transitions in a given compound and also from one compound to another are quite reasonable, but their absolute values are in rather poor agreement with experiment. This may be partly due to solvent effects on these doubly charged species.

Perhaps the most important contribution from the numerical calculations is the prediction of energies of $n\pi^*$ states, about which the perimeter model provides no information and which are elusive experimentally. Unfortunately, they should be particularly sensitive to sovlent effects and in the aqueous solutions used could well occur at substantially higher energies than calculated. It should also be noted that all of the low-energy $n\pi^*$ transitions are forbidden by symmetry and the lowest allowed $n\pi^*$ transition occurs in a region of substantial $\pi\pi^*$ absorption and is therefore likely to be completely obscured. Finally, although the INDO/S method used gives good results for $n\pi^*$ states of neutral aza heterocycles,[19] it is not clear how well it performs for charged molecules such as those considered presently. It should be noted

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that extended Hückel calculations[16] also suggest that the lowest energy transitions are of the $n\pi^*$ type. This method is undoubtedly even less reliable for predicting energies of $n\pi^*$ type transitions.

Conclusions

We believe that as a result of this work the low-energy allowed $\pi\pi^*$ transitions, as well as some of the low-energy forbidden $\pi\pi^*$ transitions, have now been identified in the spectra of the oxocarbon dianions **1–4** and are reasonably well understood. Calculations indicate that many $n\pi^*$ transitions are also present at low energies, but their identification in experimental spectra is difficult.

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Experimental and Theoretical Evidence for Double Bonds between Metal Atoms. Dinuclear Alkoxo-Bridged Ditungsten(IV,IV) Complexes, $W_2Cl_4(OR)_4(ROH)_2$

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Abstract: The two compounds of general formula $W_2Cl_4(OR)_4(HOR)_2$ with R = CH_3 (**1**) and R = C_2H_5 (**2**) have been prepared from W_2(2,4-dimethyl-6-oxopyrimidinate)$_4$. A range of physical techniques, including X-ray crystallography and molecular orbital calculations by the Fenske–Hall method, has been used to characterize them, especially with regard to the bonding between the metal atoms. Crystals of **1** belong to the space group $P2_1/n$ with a = 7.219 (1) Å, b = 9.459 (1) Å, c = 12.047 (1) Å, β = 96.127 (9)°, V = 818.1 (3) Å^3, and Z = 2. Crystals of **2** belong to space group $P2_1/c$ with a = 13.121 (1) Å, b = 9.935 (1) Å, c = 18.737 (2) Å, β = 99.31 (1)°, V = 2410 (4) Å^3, and Z = 4. The structures refined to R_1 = 0.023 and 0.044 and R_2 = 0.033 and 0.055 for **1** and **2**, respectively. The structures are essentially identical, consisting of two distorted octahedra sharing an edge. There is a central $Cl_2W(\mu\text{-}OR)_2WCl_2$ unit which is planar except for the R groups, and the four other RO and ROH ligands are placed above and below this plane to complete the distorted octahedra. On each side of the central plane there is one RO and one ROH ligand which are presumably hydrogen bonded since the O···O distances are ca. 2.49 Å. The tungsten–tungsten distances are 2.481 (1) Å in **1** and 2.483 (1) Å in **2**. The metal–metal bond is of formal order 2 and consists of a π bond provided by the HOMO ($11b_u$) and a σ bond provided partly by the highest ($10a_g$) and another ($7a_g$) totally symmetric MO's. The electrochemistry of **2** is consistent with its facile oxidation to the W–W single-bond compound $W_2Cl_4(OEt)_6$. The implications of the present results for a number of other oxo-bridged binuclear systems are briefly discussed.

The question of whether direct metal–metal bonds really exist in bridged dinuclear species, even when magnetic measurements imply that internuclear coupling of electron spins occurs, has been debated for a long time.[2] The compounds we have characterized here, $W_2Cl_4(OR)_4(ROH)_2$, with R = CH_3 and C_2H_5, afford an excellent focus for discussion. The fact that the metal atoms are close together would tend to persuade nearly everyone that there is some direct metal–metal bonding, but there remains the question of whether the bond order is 1 or 2. It could be contended that there is only one direct (presumably σ) bond between the metal atoms and that the spins of the remaining two electrons get coupled by some form of molecular orbital delocalization through the bridging groups. Still other hypotheses are possible. Some nonempirical MO calculations were therefore considered worthwhile not only to give us an understanding of the specific molecules under consideration but for more general reasons.

Our concern with the electronic structures of these molecules was a serendipitous result of an attempt to develop a strategy for the synthesis of the elusive octachloroditungstate(II) anion. We explored the feasibility of converting the quadruply bonded ditungsten complex $W_2(mhp)_4$ (mhp is the anion of 2-hydroxy-6-methylpyridine) to $[W_2Cl_8]^{4-}$ through its reaction with gaseous hydrogen chloride in alcohol solvents.[3] Although unsuccessful in this our original objective, we did discover that this reaction is a very convenient synthetic route to the class of dinuclear complexes which were first formulated by Clark and Wentworth[4] as the green tungsten(III) complexes $W_2Cl_4(OR)_2(ROH)_4$. Following the work of Clark and Wentworth, others,[5,6] using different synthetic procedures, described dark green tungsten(IV) compounds $W_2Cl_4(OR)_4(ROH)_2$, the stoichiometric formulation of which differs from $W_2Cl_4(OR)_2(ROH)_4$ by only two hydrogen atoms. Since the properties of these materials are so similar,[3–6] we considered it likely that they actually constitute a single class of complex, either being derivatives of tungsten(III) or tungsten(IV).

The course of the present investigation therefore shaped itself to the following objectives: (1) to confirm as far as is possible that the spectroscopic properties of the samples from the different procedures are identical; (2) to characterize these molecules structurally by x-ray crystallography; (3) to carry out theoretical studies of the tungsten–tungsten bonding by using the structural data. Our results confirm that these complexes are all members

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