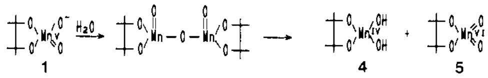
of α-ketol formation in aqueous solution, and it was pointed out that the disproportionation proceeds very rapidly via protonation and dimerization from analogy with inorganic manganate(V), as in eq 3. From this point of view, the stability of the manganate(V)



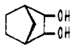
1 4 5 (3)

diester **1** in the nonaqueous solvent can be explained in terms of the tight ion pair formation[1] with quaternary ammonium ion in the solvent cage that obstructs the dimerization.

The Mn(VI) ester **5** thus formed undergoes a rapid oxidative decomposition to give the dialdehyde **3** and MnO_2 but escapes reaction with iodide due to its short lifetime. On the other hand, the Mn(IV) ester **4** has a longer lifetime and reacts with iodide to give Mn(II) and the diol **2**. Consequently, this mechanism well explains the **3**/**2** ratio observed after the titration. Since only Mn(IV) (including MnO_2 formed from **5** by the oxidative decomposition) reacts with iodide, the mechanism is also consistent with the results of the titration.

The rapid decrease in the **3**/**2** ratio and the little change in the apparent oxidation state observed in the first 10 min (Table I), when considered with the kinetic results, indicate that the spectral change (Figure 1) is a result of the subsequent reduction of the manganate(V) ester ion **1** to a manganese(IV) species, probably by abstraction of a hydrogen atom from the excess alkene as shown Scheme Ib. Since the spectrum e (Figure 1) resembles that of a colloid,[22] the initial products of this reaction may be manganese dioxide and the alkoxide ion of **2**.

The subsequent slow increase in the **3**/**2** ratio and slow decrease in the apparent oxidation state are due to oxidation of **2** to **3** by resulting MnO_2, because separately added *exo-cis*-bicyclo[2.2.1]heptane-2,3-diol (**6**) was also converted slowly to a cor-



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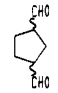

7

responding dialdehyde **7** in the colloidal solution obtained by the reaction of permanganate with DCPD. In these experiments the dialdehydes **3** and **7** were obtained as a mixture of isomers due to the presence of the alkoxide ion of **2**.

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[22] The plot of log (absorbance) vs log λ for this spectrum shows a linear relationship with a slope of -4.3 as expected by Raileigh's law (absorbance $= C/\lambda^4$) for colloidal solution where the energy loss is due to light scattering.[20]

Chemistry, Structure, and Bonding in Diruthenium(II) Tetracarboxylates

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Contribution from the Department of Chemistry and Laboratory for Molecular Structure and Bonding, Texas A&M University, College Station, Texas 77843, and Contribution No. 7896 from the Arthur Amos Noyes Laboratory, California Institute of Technology, Pasadena, California 91109. *Received January 4, 1989*

Abstract: $Ru_2(O_2CCH_3)_4Cl$ reacts with L-mandelic acid (Hmand) to convert 50% of the ruthenium to $Ru_2(mand)_4(H_2O)_2$ (**2**) and 50% to the accompanying disproportionation product, $[Ru_3O(mand)_6(H_2O)_3]^+$. The Ru₂(II,II) mandelate has been isolated and structurally characterized as $Ru_2(mand)_4{\cdot}2H_2O$, which crystallizes in space group $P2_1$ with the following unit cell parameters: $a = 7.610$ (2) Å, $b = 32.181$ (7) Å, $c = 13.587$ (4) Å, $\beta = 90.28$ (2)°, $V = 3328$ (3) Å^3, $Z = 4$. Two independent but essentially identical molecules having mandelate ions of the correct absolute chirality were found. The Ru–Ru distances are 2.266 (1) and 2.256 (1) Å; the water molecules are axially coordinated with a mean Ru–O distance of 2.35 Å. This is the first time a Ru_2(II,II) compound has been obtained directly, on a preparative scale from a Ru_2(II,III) compound. Compound **2** can be used to prepare other Ru_2(II,II) compounds, e.g., $Ru_2(O_2CC_6H_5)_4$ (**4**) and $Ru_2(O_2CCPh_3)_4$ (**5**) in good yield. Preliminary spectroscopic results on **2** are also reported. The magnetic susceptibilities of **4** and $Ru_2(O_2CCH_3)_4$ (**6**) have been measured in the temperature range 6–298 K. The derived magnetic moments drop from ca. 3.0 μ_B at room temperature to an extrapolated value of 0 μ_B at 0 K, and the shape of the curve can be fitted by an equation derived by postulating that a $^3A_{2g}$ state, derived from a $\sigma^2\pi^4\delta^2\delta^{*2}\pi^{*2}$ configuration, undergoes a second-order splitting to give a nonmagnetic ground state ($S_z = 0$) lying 215 (25) or 244 (10) cm^{-1} for **4** and **6**, respectively, below a state with $S_z = \pm1$, while all other spin singlet states arising from the same configuration lie ca. 3000 cm^{-1} higher. This evidence for a $\sigma^2\pi^4\delta^2\delta^{*2}\pi^{*2}$ configuration is fully supported by structural relationships between the $Ru_2(O_2CR)_4^+$, $Ru_2(O_2CR)_4$, and $Ru_2(RNNNR)_4$ compounds.

Of all of the multiply bonded dimetal compounds[2] those of ruthenium have shown perhaps the most interesting variety of electronic structures. The major factor giving rise to this variety is the sensitivity of the relative energies of the two types of M–M antibonding orbitals, δ^* and π^*, which are—or can be—occupied in the Ru_2^{n+} units. The first authentic[3] diruthenium compounds reported (1966) were of the type $Ru_2(O_2CR)_4Cl$,[4,5] although their true nature was not recognized[6] until several years after the report[4] of their preparation (1969). It was then 6 more years until detailed experimental data on their electronic structures was obtained,[7] and it was not until 1979 that a full and rigorous theoretical study was published.[8] Subsequently, there have been extensive spec-

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[1] (1) Texas A&M University. (b) California Institute of Technology.

[2] (2) (a) Cotton, F. A.; Walton, R. A. *Multiple Bonds Between Metal Atoms*; Wiley: New York, 1982. (b) Cotton, F. A.; Walton, R. A. *Struct. Bonding* **1985**, *62*, 1–50.

[3] (3) In ref 4 the possibility that other types of $Ru_2(O_2CR)_2^{x+}$ compounds had been made was also tentatively advanced, but all of these others have either been shown to be something else (e.g., $[Ru_3O(O_2CR)_6(H_2O)]_6^+$ in some cases[5]) or have remained ill-defined.

[4] (4) Stephenson, T. A.; Wilkinson, G. *J. Inorg. Nucl. Chem.* **1966**, *28*, 2285–2291.

[5] (5) Cotton, F. A.; Norman, Jr., J. G. *Inorg. Chim. Acta* **1972**, *6*, 411–419.

[6] (6) Bennett, M. J.; Caulton, K. G.; Cotton, F. A. *Inorg. Chem.* **1969**, *8*, 1.

[7] (7) Cotton, F. A.; Pedersen, E. *Inorg. Chem.* **1975**, *14*, 388.

[8] (8) Norman, J. G.; Renzoni, G. E.; Case, D. A. *J. Am. Chem. Soc.* **1979**, *101*, 5256–5267.

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troscopic studies[9-12] of the $Ru_2(O_2CR)_4X$ type compounds and, on the whole, their electronic structures are pretty well understood. Concerning their preparation by the reaction of $RuCl_3 \cdot nH_2O$ with a $RCO_2H/(RCO)_2O$ mixture, one question remains, however: By what agent is some of the Ru^{III} reduced to Ru^{II}?

In contrast to this lengthy, but ultimately thorough, process of elucidating the nature of the $Ru_2(O_2CR)_4^+$ species, work bearing on the possible existence of $Ru_2(O_2CR)_4^{2+}$ and $Ru_2(O_2CR)_4$ species has lagged until quite recently. With respect to the former, their existence now seems unlikely;[13] in any event none have yet been authenticated,[13] although several claims of their preparation have been advanced.[14,15]

Turning now to the $Ru_2(O_2CR)_4$ compounds, their existence in isolable form was clearly adumbrated in 1975 by the observation[7] of a reversible reduction of $Ru_2(O_2CC_3H_7)_4Cl$ at a voltage of only -0.36 V vs SCE. These elusive compounds were not reported, however, until 10 years later.[16,17] They proved, as expected, to be quite stable. In this paper we report some structural and magnetic studies we have made on $Ru_2(O_2CR)_4$ compounds with a view to establishing with greater certainty the ground-state electron configuration. The presence of two unpaired electrons at room temperature, as already reported,[16,17] is equally compatible with $\sigma^2\pi^4\delta^2\delta^*\pi^{*3}$, $\sigma^2\pi^4\delta^2\delta^{*2}\pi^{*2}$, and $\sigma^2\pi^4\delta^2\pi^{*3}\delta^*$ configurations, where the first and the last are different in having the δ^* level slightly below and slightly above the π^* level, respectively. The second one would arise only if the δ^* level is appreciably below the π^* level. A fourth possibility, $\sigma^2\pi^4\delta^2\pi^{*4}$, is ruled out because it would give a diamagnetic ground state. We shall present evidence here that convincingly establishes the ground state as one arising from the $\sigma^2\pi^4\delta^2\delta^{*2}\pi^{*2}$ configuration. We shall also describe a synthetic route to several $Ru_2(O_2CR)_4$ compounds that is quite different from the one previously published.[16,17]

Experimental Section

$Ru_2(O_2CCH_3)_4Cl$ was prepared by using a literature method from $RuCl_3 \cdot 3H_2O$.[4]. The yield was 81%.

Reaction of $Ru_2(O_2CCH_3)_4Cl$ with L-Mandelic Acid. $Ru_2(O_2CCH_3)_4Cl$ (1.7 mmol) and L-mandelic acid (42 mmol) were refluxed in H_2O (200 mL) in a 100-mL flask and under an Ar atmosphere for 1.5 h. A yellow precipitate (**1**) was formed in a period of 5 min and then disappeared to give a green-brown solution in a period of 1 h. When the solution was cooled slowly, a good crop of flat, golden crystals of **2**, which was characterized via X-ray structure analysis as $Ru_2[L\text{-}O_2CCH(OH)C_6H_5]_4 \cdot 2H_2O$, came out, and a green solution, **3**, was left. The yield of **2** was about 50% based on $Ru_2(O_2CCH_3)_4Cl$. The single crystals of **2** used for structure determination were made in a more dilute solution by using the same procedures.

Preparation of $Ru_2(O_2CPh)_4(H_2O)_{1.2}(EtOH)_{0.8}$ (4). Compound **2** (1.0 g) and HO_2CPh (6.0 g) were refluxed in EtOH in an atmosphere of Ar for 2 h, giving rise to a brown crystalline product, **4**, in a yield of 80%. The product was washed with small portions of EtOH and dried in vacuum. The chemical analysis suggested the formula $Ru_2(O_2CPh)_4(H_2O)_{1.2}(EtOH)_{0.8}$. The electronic spectrum of **4** shows a shoulder at about 440 nm.

Preparation of $Ru_2(O_2CCH_3)_4$. This compound was made from the "blue solution" by using a literature method.[16] The yield was 52%.

Physical Measurements. The electronic absorption spectra were obtained on a Cary 17D spectrophotometer. The CD spectrum was taken on a Cary 60 spectropolarimeter. Elemental microanalysis was performed by Galbraith Laboratories, Inc., Knoxville, TN. The magnetic susceptibility measurements were made at the University of Southern California SQUID Instrumentation Facility (supported by NSF Grant CHE82-11349). ESR spectra could not be observed at ca. 70 K for $Ru_2(O_2CCPh_3)_4$ either in crystalline form or doped into the isomorphous molybdenum compound at the 1% level. Solutions of the mandelate compounds of the II, III and II, II type were examined at ca. 70 K in frozen ethanol solution, whereby a spectrum was seen for the former but not for the latter.

Table I. Crystallographic Data for **2**.

chem formula	$Ru_2C_{32}H_{32}O_{14}$	Z	4
formula wt	842.74	T, °C	20
space group	$P2_1(4)$	λ, Å	0.71073
a, Å	7.610 (2)	ρ_{calcd}, g cm^{-3}	1.682
b, Å	32.181 (7)	μ, cm^{-1}	9.60
c, Å	13.587 (4)	trans coeff	obsd 0.82-1.00
β, deg	90.28 (2)	$R(F_o)$	0.042
V, Å^3	3328 (3)	$R_w(F_o)$	0.053

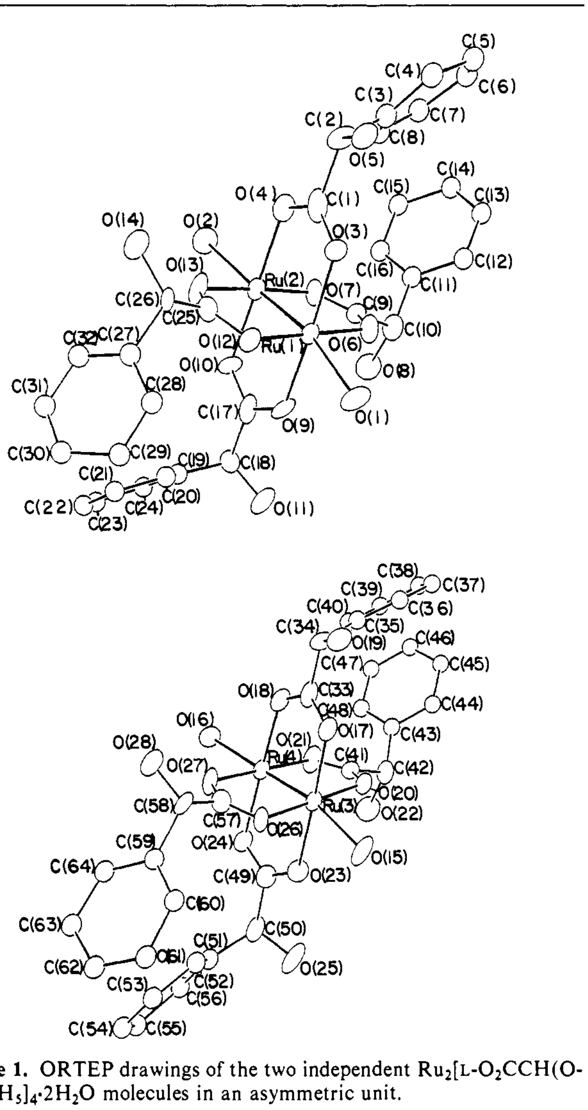

Figure 1. ORTEP drawings of the two independent $Ru_2[L\text{-}O_2CCH(OH)C_6H_5]_4 \cdot 2H_2O$ molecules in an asymmetric unit.

X-ray Crystallography. The crystal structure of **2** was obtained by using the general procedures described elsewhere.[18] The refinement of the S enantimorph gave a lower R value than that for the R enantimorph, in agreement with the use of the L-mandelic acid, which has the S configuration. The crystal parameters and the information concerning the data collection and structure refinement are summarized in Table I.

Results

Preparation and Reactions of Ru_2(L-mandelate)$_4$. The golden crystals of **2**, which resulted from the reaction of $Ru_2(O_2CCH_3)_4Cl$ with L-mandelic acid, were found to have a much lower magnetic susceptibility than would be expected for a Ru$_2$(II,III) carboxylate which would have resulted from a simple ligand-exchange reaction.

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(9) Martin, D. S.; Newman, R. A.; Vlasnik, L. M. *Inorg. Chem.* **1980**, *19*, 3404-3407.

(10) Clark, R. J. H.; Ferris, L. T. H. *Inorg. Chem.* **1981**, *20*, 2759-2766.

(11) Miskowski, V. M.; Loehr, T. M.; Gray, H. B. *Inorg. Chem.* **1987**, *26*, 1098-1108.

(12) Miskowski, V. M.; Gray, H. B. *Inorg. Chem.* **1988**, *27*, 2501-2506.

(13) Cotton, F. A.; Matusz, M.; Zhong, B. *Inorg. Chem.* **1988**, *27*.

(14) Drew, M. G. B.; Higgins, P.; McCann, G. M. *J. Chem. Soc., Chem. Commun.* **1987**, 1385.

(15) Higgins, P.; McCann, G. M. *J. Chem. Soc., Dalton. Trans.* **1988**, 661-667.

(16) Lindsay, A. J.; Wilkinson, G.; Motevalli, M.; Hursthouse, M. B. *J. Chem. Soc., Dalton Trans.* **1985**, 2321-2326.

(17) Lindsay, A. J.; Wilkinson, G.; Motevalli, M.; Hursthouse, M. B. *J. Chem. Soc., Dalton Trans.* **1987**, 2723-2736.

(18) Bino, A.; Cotton, F. A.; Felthouse, T. R. *Inorg. Chem.* **1979**, *18*, 2599.

Table II. Positional Parameters and Their Estimated Standard Deviations for Ru_2(L-mandelate)$_4$·$2H_2O$[a]

atom	*x*	*y*	*z*	*B*, (Å^2)	atom	*x*	*y*	*z*	*B*, (Å^2)
Ru(1)	0.6685 (1)	0.570	0.89727 (7)	1.77 (2)	C(17)	0.563 (2)	0.5232 (4)	1.0721 (9)	2.3 (3)
Ru(2)	0.8510 (1)	0.57879 (3)	1.02767 (7)	1.83 (2)	C(18)	0.449 (2)	0.4947 (4)	1.136 (1)	2.4 (3)
Ru(3)	1.3704 (1)	0.57482 (3)	1.39725 (7)	1.80 (2)	C(19)	0.546 (2)	0.4531 (4)	1.144 (1)	2.8 (3)*
Ru(4)	1.1875 (1)	0.56492 (3)	1.52615 (7)	1.83 (2)	C(20)	0.602 (2)	0.4322 (5)	1.063 (1)	4.0 (3)*
O(1)	0.462 (1)	0.5474 (3)	0.7773 (7)	3.3 (2)	C(21)	0.684 (3)	0.3926 (6)	1.078 (2)	5.8 (4)*
O(2)	1.048 (1)	0.5897 (3)	1.1571 (6)	3.1 (2)	C(22)	0.692 (3)	0.3764 (6)	1.170 (2)	5.9 (5)*
O(3)	0.832 (1)	0.6073 (3)	0.8144 (6)	2.1 (2)	C(23)	0.640 (3)	0.3966 (6)	1.250 (1)	5.4 (4)*
O(4)	1.001 (1)	0.6182 (3)	0.9462 (6)	2.5 (2)	C(24)	0.561 (2)	0.4359 (5)	1.241 (1)	4.2 (3)*
O(5)	1.059 (1)	0.6477 (3)	0.6978 (6)	2.6 (2)	C(25)	0.960 (2)	0.5133 (4)	0.897 (1)	2.4 (3)
O(6)	0.521 (1)	0.6203 (3)	0.9382 (6)	2.5 (2)	C(26)	1.084 (2)	0.4833 (4)	0.8464 (9)	1.9 (3)
O(7)	0.687 (1)	0.6262 (3)	1.0752 (7)	2.6 (2)	C(27)	1.041 (2)	0.4376 (4)	0.862 (1)	2.3 (2)*
O(8)	0.333 (1)	0.6437 (3)	1.1479 (7)	3.2 (3)	C(28)	0.904 (2)	0.4208 (5)	0.805 (1)	3.9 (3)*
O(9)	0.515 (1)	0.5326 (3)	0.9846 (7)	2.4 (2)	C(29)	0.856 (2)	0.3783 (6)	0.815 (1)	5.1 (4)*
O(10)	0.700 (1)	0.5393 (3)	1.1139 (6)	2.4 (2)	C(30)	0.968 (2)	0.3526 (6)	0.881 (1)	4.6 (4)*
O(11)	0.289 (1)	0.4893 (3)	1.0822 (7)	3.4 (2)	C(31)	1.091 (2)	0.3715 (5)	0.936 (1)	4.6 (4)*
O(12)	0.810 (1)	0.5190 (3)	0.8522 (6)	2.3 (2)	C(32)	1.132 (2)	0.4142 (5)	0.925 (1)	4.0 (3)*
O(13)	1.003 (1)	0.5302 (3)	0.9751 (7)	2.7 (2)	C(33)	1.086 (2)	0.5185 (4)	1.3531 (9)	2.1 (3)
O(14)	1.263 (1)	0.4926 (3)	0.8735 (7)	2.9 (2)	C(34)	0.978 (2)	0.4865 (4)	1.2990 (9)	2.2 (3)
O(15)	1.576 (1)	0.5964 (3)	1.2771 (6)	3.4 (2)	C(35)	1.050 (2)	0.4442 (4)	1.321 (1)	3.1 (3)*
O(16)	0.992 (1)	0.5541 (3)	1.6551 (6)	2.7 (2)	C(36)	1.107 (2)	0.4172 (5)	1.247 (1)	4.4 (4)*
O(17)	1.210 (1)	0.5362 (3)	1.3124 (6)	2.4 (2)	C(37)	1.186 (3)	0.3780 (7)	1.267 (2)	6.7 (5)*
O(18)	1.044 (1)	0.5239 (3)	1.4419 (7)	2.6 (2)	C(38)	1.189 (3)	0.3665 (6)	1.365 (2)	6.2 (5)*
O(19)	0.988 (1)	0.4948 (3)	1.1966 (7)	3.1 (2)	C(39)	1.140 (3)	0.3925 (6)	1.441 (1)	5.5 (4)*
O(20)	1.517 (1)	0.5242 (3)	1.4405 (6)	2.2 (2)	C(40)	1.066 (2)	0.4305 (5)	1.419 (1)	3.9 (3)*
O(21)	1.351 (1)	0.5174 (3)	1.5744 (6)	2.5 (2)	C(41)	1.483 (2)	0.5087 (4)	1.5230 (9)	1.9 (3)
O(22)	1.702 (1)	0.4997 (3)	1.6486 (7)	3.5 (2)	C(42)	1.628 (2)	0.4793 (4)	1.562 (1)	2.7 (3)
O(23)	1.522 (1)	0.6119 (3)	1.4867 (6)	2.3 (2)	C(43)	1.556 (2)	0.4375 (4)	1.593 (1)	3.3 (3)*
O(24)	1.337 (1)	0.6060 (3)	1.6134 (6)	2.3 (2)	C(44)	1.617 (2)	0.4034 (5)	1.538 (1)	4.3 (3)*
O(25)	1.756 (1)	0.6508 (4)	1.5868 (8)	4.2 (2)	C(45)	1.557 (3)	0.3628 (6)	1.562 (1)	5.3 (4)*
O(26)	1.225 (1)	0.6249 (3)	1.3531 (6)	2.3 (2)	C(46)	1.440 (2)	0.3574 (6)	1.636 (1)	5.1 (4)*
O(27)	1.031 (1)	0.6124 (3)	1.4715 (6)	2.4 (2)	C(47)	1.381 (2)	0.3909 (6)	1.692 (1)	5.0 (4)*
O(28)	0.776 (1)	0.6509 (3)	1.3754 (7)	2.9 (2)	C(48)	1.437 (2)	0.4310 (5)	1.668 (1)	3.7 (3)*
C(1)	0.958 (2)	0.6236 (4)	0.8591 (9)	2.4 (3)	C(49)	1.476 (2)	0.6202 (4)	1.575 (1)	2.2 (3)
C(2)	1.073 (2)	0.6556 (4)	0.8014 (9)	2.2 (3)	C(50)	1.591 (2)	0.6487 (5)	1.635 (1)	2.9 (3)
C(3)	1.018 (2)	0.6993 (4)	0.824 (1)	2.8 (3)*	C(51)	1.515 (2)	0.6908 (5)	1.646 (1)	3.4 (3)*
C(4)	1.028 (3)	0.7295 (7)	0.753 (2)	6.2 (5)*	C(52)	1.442 (2)	0.7111 (5)	1.564 (1)	4.5 (4)*
C(5)	0.966 (3)	0.7694 (7)	0.775 (2)	7.4 (6)*	C(53)	1.388 (3)	0.7528 (8)	1.572 (2)	8.0 (6)*
C(6)	0.917 (3)	0.7812 (7)	0.862 (2)	6.5 (5)*	C(54)	1.401 (3)	0.7735 (7)	1.659 (2)	6.8 (5)*
C(7)	0.920 (3)	0.7521 (6)	0.941 (2)	6.0 (5)*	C(55)	1.477 (3)	0.7555 (8)	1.737 (2)	7.5 (6)*
C(8)	0.967 (2)	0.7108 (5)	0.921 (1)	4.0 (3)*	C(56)	1.529 (3)	0.7112 (6)	1.735 (1)	5.4 (4)*
C(9)	0.555 (2)	0.6351 (4)	1.0208 (9)	1.9 (3)	C(57)	1.079 (2)	0.6304 (4)	1.393 (1)	2.5 (3)
C(10)	0.409 (2)	0.6638 (4)	1.064 (1)	2.6 (3)	C(58)	0.953 (2)	0.6608 (4)	1.346 (1)	2.4 (3)
C(11)	0.478 (2)	0.7072 (4)	1.089 (1)	2.7 (3)*	C(59)	0.998 (2)	0.7053 (4)	1.362 (1)	2.5 (3)*
C(12)	0.419 (2)	0.7408 (5)	1.032 (1)	4.1 (3)*	C(60)	1.122 (2)	0.7252 (5)	1.304 (1)	4.4 (4)*
C(13)	0.476 (3)	0.7807 (6)	1.056 (2)	6.1 (5)*	C(61)	1.162 (3)	0.7678 (6)	1.313 (1)	6.0 (5)*
C(14)	0.587 (3)	0.7877 (6)	1.135 (2)	6.3 (5)*	C(62)	1.067 (3)	0.7899 (6)	1.381 (2)	6.2 (5)*
C(15)	0.652 (2)	0.7542 (6)	1.195 (1)	4.9 (4)*	C(63)	0.939 (3)	0.7721 (6)	1.445 (1)	5.4 (4)*
C(16)	0.590 (2)	0.7138 (5)	1.171 (1)	4.1 (3)*	C(64)	0.908 (2)	0.7286 (5)	1.432 (1)	4.7 (4)*

[a] Starred atoms were refined isotropically.

The magnetic moment at room temperature of 3.0 μ_B per dimer indicated that each dimer has two unpaired electrons and that a Ru_2(II,III) carboxylate had been converted to a Ru_2(II,II) one. The electronic spectrum of **2** shows a peak at 443 nm (ϵ 495), which also suggested a Ru_2(II,II) carboxylate. These observations led us to carry out an X-ray structure analysis, which confirmed this conclusion. As shown in Figure 1, the compound is Ru_2[L-$O_2CCH(OH)C_6H_5$]$_4$·$2H_2O$, and there are two independent molecules in the asymmetric unit. All mandelate ligands in these molecules have an *S* conformation, the same one as that of L-mandelic acid. The positional parameters and the bond distances and angles are given in Table II–IV. These structural results will be discussed in detail later.

The preparative reaction seemed likely to be a disproportionation since there was no independent reducing agent in the reaction mixture. When the green solution (**3**) was concentrated, a mixture of a green powder and colorless crystals of L-mandelic acid was obtained; the green solution and powder was then presumed to be the other (Ru^{III}) disproportionation product. Several careful runs of the reaction resulted in a reproducible yield of approximately 50% of the diruthenium(II,II) mandelate based on starting $Ru_2(O_2CCH_3)_4Cl$.

To identify the green product, it was necessary to separate it from the excess mandelic acid. While this was problematical because of their similar solubilities in most solvents, it was found that the mandelic acid is quite soluble in acetic acid while the green powder is virtually insoluble. The pure green powder so obtained could still not be crystallized, but its visible spectrum (770 nm (1225), 590 nm (960), 335 nm (sh, ca. 1330)) and its magnetic susceptibility suggest that it is of the well-known[19] oxo-centered trimer type, namely, $[Ru_3O(O_2CR)_6(H_2O)_3]RCO_2$, where RCO_2 = L-$(C_6H_5)(HO)HCCO_2$.

It seems, therefore, that the reaction consists of two steps. The first one would be a simple carboxylate-exchange reaction resulting in Ru_2[L-$O_2CCH(OH)C_6H_5$]$_4$Cl, which may be the yellow precipitate observed in the early period of reaction. The second step would be the disproportionation of Ru_2[L-$O_2CCH(OH)C_6H_5$]Cl. In agreement with this, we found that a high concentration of Cl^- (addition of excess LiCl) caused the reaction to stop at the yellow precipitate (**1**). Compound **1** has a peak at 430 nm (755) in its electronic spectrum and has a magnetic moment 4.1 μ_B per dimer, which indicates three unpaired electrons per dimer as expected for Ru_2[L-$O_2CCH(OH)C_6H_5$]$_4$Cl. The overall reaction of $Ru_2(O_2CCH_3)_4Cl$ with mandelic acid can presumably be represented

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[19] Spencer, A.; Wilkinson, G. *J. Chem. Soc., Dalton Trans.* **1972**, 1570. Cotton, F. A., Norman, J. G., Jr. *Inorg. Chim. Acta* **1972**, *6*, 411.

Table III. Selected Bond Distances (angstroms) for Ru_2(L-mandelate)$_4\cdot 2H_2O$[a]

atom 1–atom 2	dist	atom 1–atom 2	dist
Ru(1)–Ru(2)	2.266 (1)	Ru(4)–O(21)	2.076 (9)
Ru(1)–O(1)	2.366 (9)	Ru(4)–O(24)	2.104 (8)
Ru(1)–O(3)	2.078 (8)	Ru(4)–O(27)	2.071 (9)
Ru(1)–O(6)	2.061 (9)	O(3)–C(1)	1.25 (2)
Ru(1)–O(9)	2.048 (9)	O(4)–C(1)	1.239 (15)
Ru(1)–O(12)	2.043 (8)	O(6)–C(9)	1.245 (15)
Ru(2)–O(2)	2.330 (9)	O(7)–C(9)	1.276 (15)
Ru(2)–O(4)	2.038 (9)	O(9)–C(17)	1.277 (15)
Ru(2)–O(7)	2.074 (9)	O(10)–C(17)	1.29 (2)
Ru(2)–O(10)	2.079 (9)	O(12)–C(25)	1.31 (2)
Ru(2)–O(13)	2.075 (9)	O(13)–C(25)	1.23 (2)
Ru(3)–Ru(4)	2.265 (1)	O(17)–C(33)	1.237 (15)
Ru(3)–O(15)	2.369 (9)	O(18)–C(33)	1.261 (15)
Ru(3)–O(17)	2.085 (9)	O(20)–C(41)	1.256 (15)
Ru(3)–O(20)	2.060 (8)	O(21)–C(41)	1.255 (15)
Ru(3)–O(23)	2.056 (8)	O(23)–C(49)	1.280 (15)
Ru(3)–O(26)	2.045 (8)	O(24)–C(49)	1.27 (2)
Ru(4)–O(16)	2.332 (9)	O(26)–C(57)	1.25 (2)
Ru(4)–O(18)	2.055 (9)	O(27)–C(57)	1.27 (2)

[a] Numbers in parentheses are estimated standard deviations in the least significant digits.

Table IV. Selected Bond Angles (degrees) for Ru_2(L-mandelate)$_4\cdot 2H_2O$[a]

atom 1–atom 2–atom 3	angle	atom 1–atom 2–atom 3	angle
Ru(2)–Ru(1)–O(1)	168.6 (2)	O(15)–Ru(3)–O(26)	85.7 (3)
Ru(2)–Ru(1)–O(3)	88.8 (2)	O(17)–Ru(3)–O(20)	90.1 (3)
Ru(2)–Ru(1)–O(6)	90.9 (3)	O(17)–Ru(3)–O23)	177.3 (3)
Ru(2)–Ru(1)–O(9)	88.4 (2)	O(17)–Ru(3)–O(26)	89.6 (3)
Ru(2)–Ru(1)–O(12)	91.0 (2)	O(20)–Ru(3)–O(23)	89.3 (3)
O(1)–Ru(1)–O(3)	101.5 (3)	O(20)–Ru(3)–O(26)	179.5 (3)
O(1)–Ru(1)–O(6)	93.7 (3)	O(2)–Ru(3)–O(26)	91.1 (3)
O(1)–Ru(1)–O(9)	81.2 (3)	Ru(3)–Ru(4)–O(16)	178.0 (2)
O(1)–Ru(1)–O(12)	84.4 (3)	Ru(3)–Ru(4)–O(18)	89.2 (3)
O(3)–Ru(1)–O(6)	90.5 (3)	Ru(3)–Ru(4)–O(21)	88.7 (2)
O(3)–Ru(1)–O(9)	177.2 (3)	Ru(3)–Ru(4)–O(24)	90.9 (2)
O(3)–Ru(1)–O(12)	89.2 (3)	Ru(3)–Ru(4)–O(27)	88.4 (2)
O(6)–Ru(1)–O(9)	89.6 (3)	O(16)–Ru(4)–O(18)	89.0 (3)
O(6)–Ru(1)–O(12)	178.0 (3)	O(16)–Ru(4)–O(21)	92.1 (3)
O(9)–Ru(1)–O(12)	90.8 (3)	O(16)–Ru(4)–O(24)	90.9 (3)
Ru(1)–Ru(2)–O(2)	177.5 (2)	O(16)–Ru(4)–O(27)	90.7 (3)
Ru(1)–Ru(2)–O(4)	90.0 (3)	O(18)–Ru(4)–O(21)	91.1 (3)
Ru(1)–Ru(2)–O(7)	88.5 (3)	O(18)–Ru(4)–O(24)	179.0 (4)
Ru(1)–Ru(2)–O(10)	91.2 (2)	O(18)–Ru(4)–O(27)	88.4 (3)
Ru(1)–Ru(2)–O(13)	88.4 (3)	O(21)–Ru(4)–O(24)	87.9 (3)
O(2)–Ru(2)–O(4)	87.5 (3)	O(21)–Ru(4)–O(27)	177.1 (3)
O(2)–Ru(2)–O(7)	92.2 (3)	O(24)–Ru(4)–O(27)	92.7 (3)
O(2)–Ru(2)–O(10)	91.2 (3)	Ru(1)–O(3)–C(1)	116.3 (8)
O(2)–Ru(2)–O(13)	90.9 (3)	Ru(2)–O(4)–C(1)	117.3 (8)
O(4)–Ru(2)–O(7)	93.0 (4)	Ru(1)–O(6)–C(9)	115.8 (8)
O(4)–Ru(2)–O(10)	178.6 (3)	Ru(2)–O(7)–C(9)	117.2 (8)
O(4)–Ru(2)–O(13)	88.0 (4)	Ru(1)–O(9)–C(17)	121.0 (8)
O(7)–Ru(2)–O(10)	86.5 (3)	Ru(2)–O(10)–C(17)	116.3 (8)
O(7)–Ru(2)–O(13)	176.8 (4)	Ru(1)–O(12)–C(25)	115.6 (8)
O(10)–Ru(2)–O(13)	92.6 (3)	Ru(2)–O(13)–C(25)	118.7 (8)
Ru(4)–Ru(3)–O(15)	169.7 (3)	Ru(3)–O(17)–C(33)	118.3 (8)
Ru(4)–Ru(3)–O(17)	89.1 (2)	Ru(4)–O(18)–C(33)	119.2 (8)
Ru(4)–Ru(3)–O(20)	90.1 (2)	Ru(3)–O(20)–C(41)	117.0 (8)
Ru(4)–Ru(3)–O(23)	88.3 (2)	Ru(4)–O(21)–C(41)	117.9 (8)
Ru(4)–Ru(3)–O(26)	90.2 (2)	Ru(3)–O(23)–C(49)	121.2 (8)
O(15)–Ru(3)–O(17)	100.4 (3)	Ru(4)–O(24)–C(49)	116.4 (8)
O(15)–Ru(3)–O(20)	94.1 (3)	Ru(3)–O(26)–C(57)	117.6 (8)
O(15)–Ru(3)–O(23)	82.3 (3)	Ru(4)–O(27)–C(57)	118.1 (8)

[a] Numbers in parentheses are estimated standard deviations in the least significant digits.

by the following chemical equations (where mand represents the L-mandelate anion):

$$Ru_2(O_2CCH_3)_4Cl + 4Hmand \rightarrow Ru_2(mand)_4Cl + 4CH_3CO_2H$$

$$6Ru_2(mand)_4Cl + 8H_2O \rightarrow 3Ru_2(mand)_4 + 2[Ru_3O(mand)_6(H_2O)_3]Cl + 4HCl$$

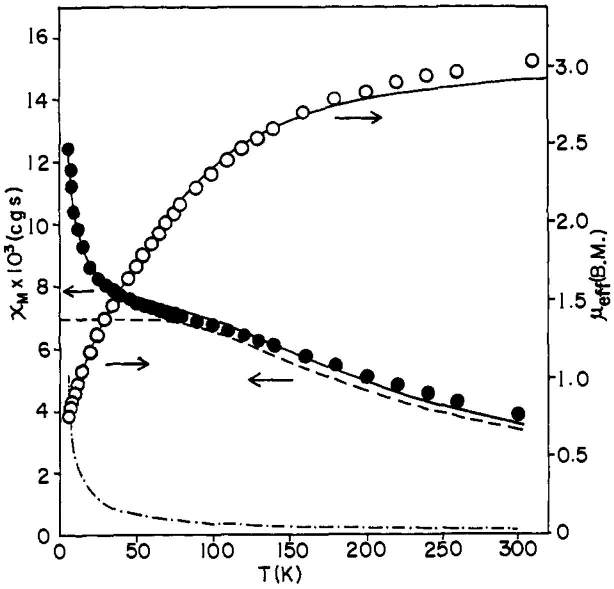

Figure 2. Magnetic susceptibility (●) and magnetic moment (○) vs T (K) for $Ru_2(O_2CC_6H_5)_4(H_2O)_{1.2}(C_2H_5OH)_{0.8}$. The correction for paramagnetic impurity is given by ·–·, and the net susceptibility (from which magnetic moments are calculated) is shown by the – – –.

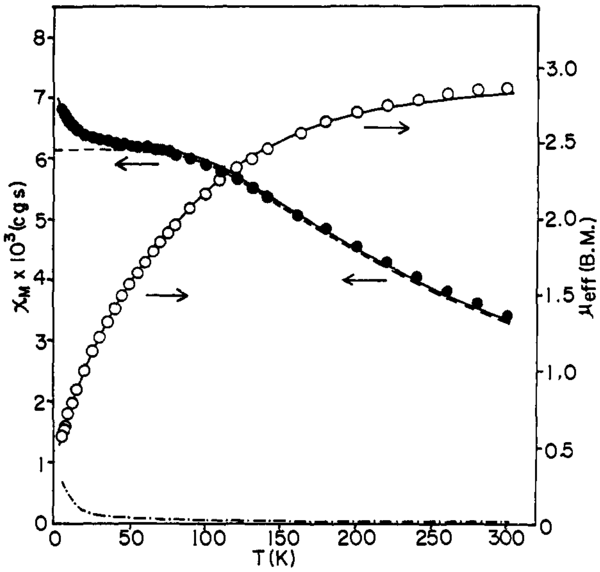

Figure 3. Magnetic susceptibility (●) and magnetic moment (○) vs. T (K) for $Ru_2(O_2CCH_3)_4$. Other features as in Figure 2.

$Ru_2[L\text{-}O_2CCH(OH)C_6H_5]_4$ is a useful starting material for synthesis of other Ru$_2$(II,II) dimers because of its good solubility in common organic solvents. Examples are the synthesis of $Ru_2(O_2CPh)_4(H_2O)_{1.2}(EtOH)_{0.8}$ (see Experimental Section) and also the synthesis of $Ru_2(O_2CCPh_3)_4\cdot H_2O\cdot EtOH$.[20] When 0.5 g of **2** and 1.16 g of HO_2CCPh_3 were refluxed in EtOH (40 mL) for 1 h, a yellow powder of $Ru_2(O_2CCPh_3)_4\cdot H_2O\cdot EtOH$ was obtained in a yield of 86%. When $Ru_2(O_2CCH_3)_4Cl$ was refluxed with NH_4Ac in water, disproportionation again occurred, and single crystals of $Ru_2(O_2CCH_3)_4\cdot 2H_2O$ were formed in very low yield when the solution was cooled. Their identity was verified by crystal structure analysis, which gave results in agreement with those reported by Wilkinson et al.[16]

Magnetic Studies. It is primarily through magnetic studies that we have been led to the conclusion that $Ru_2(O_2CR)_4$ compounds have a $\sigma^2\pi^4\delta^2\delta^{*2}\pi^{*2}$ electronic configuration, but, as will be noted later, it would also be difficult to account for the invariance of

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(20) Full structural characterization of this compound will be reported later along with structural data on some other $M_2(O_2CCPh_3)_4$ compounds.

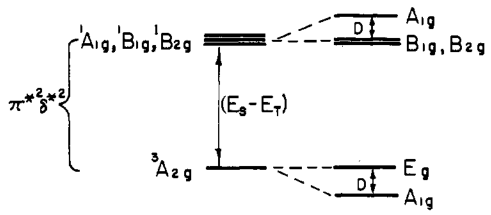

Figure 4. Diagram of the states arising from a π^{*2} configuration, with the large primary singlet–triplet separation ($E_S - E_T$) and the smaller second-order splitting of the $^3A_{2g}$ ground state (D).

Ru–Ru bond length from the II, III to the II, II compounds in any other way.

The magnetic susceptibilities of two compounds, $Ru_2(O_2CCH_3)_4$ and $Ru_2(O_2CC_6H_5)_4(H_2O)_{1.2}(C_2H_5OH)_{0.8}$, which we shall henceforth refer to simply as the acetate and the benzoate, have been measured from 6 to 300 K. In Figures 2 and 3 these results are presented graphically. Numerical data are included in the Supplementary Material (see paragraph at the end of the paper). The χ_M values were obtained in the usual way from the measured χ_g values, and fixed molar diamagnetic corrections (calculated from Pascal constants) of -169×10^{-6} and -285×10^{-6} cgs units were applied for the acetate and benzoate, respectively. Potentially these could have been left as parameters to be adjusted with some improvement of the fit. The accuracy of the benzoate results is limited by some uncertainty in the composition and hence in the formula weight. The formula used, in which the axial sites are postulated to be occupied by $(H_2O)_{1.2}(C_2H_5OH)_{0.8}$, is based on analytical results for C and H but could be off by perhaps ±0.2 in the subscripts.

It can be seen that there is in each case a sharply rising tail at low temperature in the plot of χ_M vs T (K). This is a very common occurrence in measurements of this nature and indicates the presence of a small amount of paramagnetic impurity that is following, at least approximately, Curie-law behavior. In the present cases we make the reasonable assumption that the impurities are the corresponding $Ru_2(O_2CR)_4^+$ species. The impurity contribution was fitted by assuming that below 35 K the apparent molar susceptibility, χ, is given by eq 1, where α is the mole

$$\chi = (1 - \alpha)\chi_0 + \alpha\chi_{imp} \tag{1}$$

fraction of Ru(II,III) impurity and values of χ_{imp} were obtained from the reported study[21] of $Ru_2(O_2CC_3H_7)_4Cl$. χ_0 is the intrinsic magnetism of the subject compound which is temperature-independent below 35 K. A simple linear least-squares fit then gave α and $(1 - \alpha)\chi_0$ from which a plot of χ_0 vs T was obtained.

The most striking feature of these results emerges when the susceptibilities are converted to μ_{eff} values. (Note that the plotted values do *not* include the correction indicated above.) The clear import of the plots of μ_{eff} vs T is that the $Ru_2(O_2CR)_4$ compounds have a nonmagnetic ground state, despite the fact that room-temperature magnetic moments imply that there are two unpaired electrons (i.e., a spin-triplet state). More specifically, the curve is of the kind expected for a spin-triplet, orbital-singlet ground-state split in such a way that a nonmagnetic component ($S_z = 0$) lies lowest with the degenerate $S_z = \pm 1$ components lying above it by an amount comparable to kT at room temperature.

There is, in fact, one (and probably only one) reasonable way to explain the existence of such a state. If we take a $\sigma^2\pi^4\delta^2\delta^{*2}\pi^{*2}$ ground configuration, the half-filled (π^{*2}) shell will give rise to the states $^1A_{1g}$, $^1B_{1g}$, $^1B_{2g}$, and $^3A_{2g}$. If the $^3A_{2g}$ lies below the others (as it might be expected to do), the presence of two unpaired electrons is accounted for. To explain why this $^3A_{2g}$ state splits to give a nondegenerate ground state with $S = 0$ (A_{1g}) that lies only about kT at room temperature (≈200 cm^{-1}) below the $S = \pm 1$ state (E_g), we invoke the qualitative picture in Figure 4. It is possible to estimate, a priori, the magnitude of D if we note (a) that overlap may be neglected because it is electron density near the nuclei that gives rise to the (relativistic) spin-orbit coupling[22] and (b) that the problem is formally similar to that for a t_{2g}^2 configuration of an octahedral complex, and thus D is given by eq 2, where λ' is the effective value of the spin-orbit

$$D = \frac{8\lambda'^2}{E_S - E_T} \tag{2}$$

coupling. Reasonable estimates of λ' and $E_S - E_T$ are 300 (see, for example, ref 23) and 3000 cm^{-1}, respectively, whereby a value of 240 cm^{-1} is estimated for D.

Having reached the above qualitative conclusions, it was necessary to see if the model could be treated satisfactorily in quantitative, parametric form. This amounts to seeing whether a fit to eq 3 can be achieved.[24] Here μ_{eff} represents the μ_{eff} values

$$(\mu_{eff})^2 = 2\bar{g}^2\left[\frac{e^{-x} + (2/x)(1 - e^{-x})}{1 + 2e^{-x}}\right] \tag{3}$$

as previously calculated at each temperature, T (K), $\bar{g}$ is an effective (isotropic) gyromagnetic ratio, and $x = D/kT$, where D is the energy difference shown in Figure 4, k is Boltzmann's constant, and T is the temperature in kelvin. It should be noted that since the plateau in χ_0 at low temperature effectively fixes the $\bar{g}^2/D$ ratio, these two parameters are strongly correlated. The solid lines in Figures 2 and 3 are the calculated values, and Table V collects the parameters used for both compounds.

Table V. Parameters[a] in Eq 1 and 2

parameter	acetate	benzoate
α (in eq 1)	0.003 (1)	0.021 (2)
χ_D (cgs units)	-169×10^{-6}	-285×10^{-6}
g	2.08 (5)	2.1 (1)
D, cm^{-1}	244 (10)	215 (25)

[a] Numbers in parentheses following values of α, g, and D are estimated standard deviations occurring in the least significant digit.

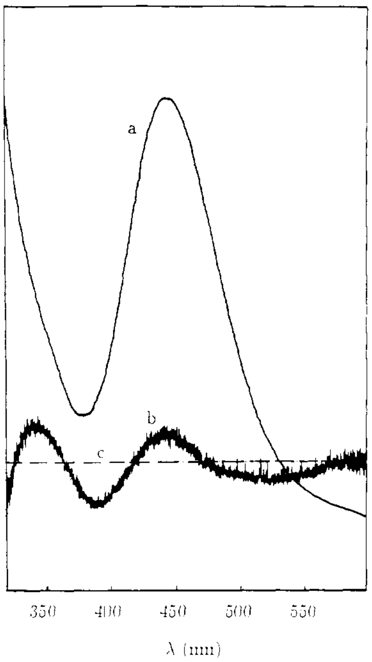

Figure 5. Electronic and circular dichroism (CD) spectra of $Ru_2[L\text{-}O_2CCH(OH)C_6H_5]_4\cdot 2H_2O$ in a THF solution of 2.25×10^{-3} M (λ_{max} in nanometers: (a) the electronic spectrum (443); (b) the CD spectrum (343, 390, 443, 534); (c) the CD base line.

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[21] Telser, J.; Drago, R. S. *Inorg. Chem.* **1984**, *23*, 3114.

[22] Ballhausen, C. J. *Molecular Electronic Structures of Transition Metal Complexes*; McGraw-Hill: New York, 1979; pp 31–36.

[23] Figgis, B. N.; Lewis, J. In *Modern Coordination Chemistry*; Lewis, J., Wilkins, R. G., Eds.; Interscience: New York 1960; see p 428.

[24] The fits were actually made to the corresponding expression for χ_M, namely, the expression obtained from eq 3 when the right-hand side is multiplied by $N\mu_B^2/3kT$.

Table VI. Lattice Parameters of $Ru_2(O_2CCH_3)_4{\cdot}2H_2O$ at Various Temperatures

T, K	a, Å	b, Å	c, Å	β, deg	V, Å^3
100	13.139	8.577	13.984	116.82	1406.4
198	13.150	8.600	13.994	116.92	1411.1
298	13.214	8.626	14.028	116.90	1425.9

It is evident that in each case a fit good enough to inspire confidence in the model is obtained but especially for the acetate where the amount of paramagnetic impurity is very small. These fits could have been further improved if the χ_D values were also treated as free parameters, but the extra effort would scarcely have been justified by any useful improvement in the numerical results, nor would it alter our conceptual picture.

The electronic spectrum of compound **2** has been studied in both the absorption and CD modes, as shown in Figure 5. In addition to the band that occurs in both the absorption and CD spectra at 450 nm, there are two other CD bands of opposite sign in the 400–500-nm region. Most likely the band at 450 nm is the electric dipole allowed Ru-O$\pi \rightarrow Ru_2\pi^*$ transition, while one of the CD satellites may be the magnetically allowed $Ru_2\sigma \rightarrow Ru_2\pi^*$ transition. We intend to study the spectra of $Ru_2(O_2CR)_4$ compounds more carefully and will not, therefore, discuss them further at this time.

Discussion

The conclusion we draw from the magnetic data, namely, that the ground states of the $Ru_2(O_2CR)_4$ molecules arise from a $\sigma^2\pi^4\delta^2\delta^{*2}\pi^{*2}$ electron configuration, is in full accord with other data on the $Ru_2(O_2CR)_4$ compounds and with the broad picture of the level orderings for Ru_2^{n+} (n = 4, 5), Rh_2^{n+} (n = 4, 5), and Pd_2^{2+} species generally.

For $Ru_2(O_2CR)_4^+$ species the presence of three unpaired electrons leads unambiguously to the conclusion that the ground state derives from a $\sigma^2\pi^4\delta^2(\delta^*\pi^*)^3$ configuration, where we use the notation $(\delta^*\pi^*)$ to indicate accidental degeneracy or near degeneracy of the δ^* and π^* orbitals. In numerous compounds containing $Ru_2(O_2CR)_4^+$ units, the Ru-Ru distances are all ca. 2.26 Å. Addition of one electron to give a $Ru_2(O_2CR)_4$ molecule would be expected (vide infra) to increase the Ru-Ru distance by ca. 0.07 Å if this electron entered a π^* orbital but to have a small or perhaps negligible effect if it entered a δ^* orbital. The observed effect is indeed negligible, so that $Ru_2(O_2CR)_4$ compounds also have Ru-Ru distances of about 2.26 Å. Thus, from this structural relationship between the $Ru_2(O_2CR)_4^+$ species where the configuration is not in doubt and the $Ru_2(O_2CR)_4$ molecules, we would conclude, in agreement with the conclusion from the magnetic measurements, that we have only two π^* electrons and, hence, a $\sigma^2\pi^4\delta^2\delta^{*2}\pi^{*2}$ ground-state configuration.

The statement made above that addition of an π^* electron should increase the Ru-Ru distance by *ca.* 0.07Å is based on the known properties of the related $Ru_2(RNNNR)_4$ compound (R = p-tolyl), where the Ru-Ru distance is 2.417 (2) Å. There are no unpaired electrons,[25] which requires a $\sigma^2\pi^4\delta^2\pi^{*4}$ ground configuration. This distance is nearly 0.16 Å longer than those in the $Ru_2(O_2CR)_4^+$ species that have $\sigma^2\pi^4\delta^2(\delta^*\pi^*)^3$ ground configurations and very comparable to those in the $Rh_2(PhNCPhNPh)_4$ and $Rh_2(tolNCHNtol)_4$ molecules (2.39-2.43 Å), which have $\sigma^2\pi^4\delta^2\pi^{*4}\delta^{*2}$ configurations.[26] The change of ligands from carboxylate to RNCHNR in rhodium compounds does not reveal any sensitivity of M-M bond length to this factor by itself. MO calculations[26,27] clearly show that the main effect of such a ligand change is to move the δ^* orbital relative to the π^* orbitals from being approximately degenerate in the carboxylate case to being ca. 1 eV higher when the more basic RNNNR or RNCRNR ligands are used.

One further point is in order with regard to the use of structural and magnetic data to indicate the correct electronic configuration. If the drop in magnetic moment from ~3.0 μ_B at room temperature toward 0 μ_B at 0 K were to be attributed to a singlet-triplet equilibrium based on states derived from different configurations, in the present case, this would have to mean a singlet ground state derived from $\sigma^2\pi^4\delta^2\pi^{*4}$ and a triplet state derived from either $\sigma^2\pi^4\delta^2\pi^{*3}\delta^*$ or $\sigma^2\pi^4\delta^2\delta^{*2}\pi^{*2}$. Because these two triplet states would have to be heavily populated at room temperature and only about half populated at 100 K and because the singlet state with its four π^* electrons should have a considerably longer Ru-Ru bond than either of the others (by ca. 0.07 and 0.15 Å, respectively), one would expect a significant *increase* in the unit cell dimensions (if not, indeed, a major reorientation of the molecules) on cooling the crystals to 100 K. We have monitored the changes, from 298 to 100 K, as reported in Table VI. The edges and volume of the unit cell all *decrease* as the temperature is lowered. The magnitude of the changes is that normally seen in molecular crystals where no significant changes in intramolecular distances are occurring, i.e., about 0.007%/K in the cell volume and by 0.0001-0.0004%/K in individual edge lengths.

In concluding, we draw attention to one aspect of the preparative work reported here. The preparation of $Ru_2[\text{L-}O_2CCH(OH)C_6H_5]_4$ from $Ru_2(O_2CCH_3)_4Cl$ is the first time that the conversion of a Ru_2(II,III) compound to a Ru_2(II,II) compound has actually been realized as a preparative procedure, although, as noted earlier, electrochemical studies long ago indicated that this should be feasible.

Acknowledgment. We thank the National Science Foundation for support of this work. We thank Professor Chris Reed and, particularly, Carol Koch, of the University of Southern California, for assistance with the magnetic measurements.

Supplementary Material Available: Complete tables of crystallographic results and tables of magnetic data (14 pages); listing of structure factors for compound **2** (19 pages). Ordering information is given on any current masthead page.

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(25) Cotton, F. A.; Matusz, M. *J. Am. Chem. Soc.* **1988**, *110*, 5761.

(26) Rizzi, G. A.; Casarin, M.; Tondello, E.; Piraino, P.; Granozzi, G. *Inorg. Chem.* **1987**, *26*, 3406.

(27) Cotton, F. A.; Feng, X. *Inorg. Chem.* **1989**, *28*, 1180.