tionalized derivatives of tetrahydrofuran with the desired absolute configuration. Showdomycin[16] was efficiently synthesized in 9 steps from **2** by the present chemicoenzymatic approach (Scheme III).

The recrystallized *tert*-butyl ester **10** was subjected to ozonolysis in ethyl acetate (−78 °C, 30 min), and the resultant solution was warmed at reflux temperatures for 1 h, affording decarboxylated cleavage product **15** in quantitative yield as an oily material. The reaction of **15** with $(EtO)_2POCH_2CN/NaH$ in absolute Me_2SO in the presence of n-Bu_4NBr under Ar atmosphere (25 °C, 6 h) affording Wittig product **16** in 61% yield from **10** as a syrup after workup and chromatography on silica gel [$[\alpha]^{20}_D$ −10.7° (c 1.0, $CHCl_3$); R_f = 0.65 (AcOEt–AcOH = 20:1)]. Reduction of **16** with diborane afforded a primary alcohol **17**[9] in 52% yield [$[\alpha]^{22}_D$ −22.2° (c 0.57, $CHCl_3$), R_f = 0.32 (AcOEt–n-hexane = 1:1)]. After acetylation of **17** with Ac_2O (**18**, 96% yield), ring closure was effected with $(CF_3CO)_2O$ (50 °C, 8 h), and removal of the protective groups with HCl in MeOH afforded showdomycin (**19**) in 30% yield from **18**. The product **19** was confirmed to be identical with authentic natural showdomycin in all respects (mixed mp, $[\alpha]_D$, IR, ^1H NMR).[17]

Cordycepin (3′-Deoxyadenosine) (22). The epoxy half-ester **5** was considered to be a chiral starting material for the synthesis of nucleosides having a different sugar moiety. Cordycepin,[18] which belongs to *N*-nucleosides with 3-deoxyribose moiety, was selected as a synthetic target. The symmetric epoxy diester **3**[5a] was treated with pig liver esterase as described in the hydrolysis of **2** to yield **5** [mp 120–122 °C, $[\alpha]^{20}_D$ −32° (c 0.50, $CHCl_3$)] in quantitative yield (Scheme I). A formal inversion of **5** to **20** was effected by treatment with excess oxalyl chloride followed by esterification[19] with t-BuOLi and alkaline hydrolysis (1 N NaOH, aqueous acetone, 5 °C, 20 min). *tert*-Butyl half-ester **20** was obtained in 56% yield from **5**, showing mp 121–124 °C, $[\alpha]^{20}_D$ +33° (c 0.5, $CHCl_3$). The successive treatment of **20** as described above (ozonolysis, Baeyer–Villiger reaction, and methanolysis) afforded **21** in a fair overall yield. Reduction of **21** with LAH gave exclusively methyl 3-deoxy-β-D-ribofuranoside in 79% yield [$[\alpha]^{20}_D$ −63° (c 0.4, $CHCl_3$)], a known precursor for cordycepin.[18] In order to determine the optical purity of **20**, the 3-deoxyribofuranoside was converted to 3′-deoxynucleoside **22** according to the procedures by Walton et al.[18] Cordycepin synthesized in 12 steps from **3** by the present study showed mp 222–224 °C, $[\alpha]^{20}_D$ −34° (c 0.25, H_2O), and was found to be about 77% ee on the basis of a reported value[18] (Scheme III).

The key features of the present methodology include the following: (1) pig liver esterase efficiently hydrolyzed unsaturated[20] meso compounds **2** and **3** with high optical purity; (2) it was found that half-esters **4** and **5** enzymatically formed correspond to the L series sugar moiety of nucleosides; the half esters were successfully transformed into the D series sugar moiety by esterification and controlled hydrolysis (**4** to **10**, and **5** to **20**); (3) a combination of chirally selective hydrolysis (enzyme process) and decarboxylative ozonolysis directly provided the versatile intermediate **15** suitable for the synthesis of *C*-nucleosides; (4) highly selective Baeyer–Villiger oxidation made possible to elaborate various types of sugar moiety including L- and D-riboses and 3-deoxyribofuranoside.

Further investigation of the present chemicoenzymatic approach to other *C*- and *N*-nucleosides and carbocyclic nucleosides are in progress in our laboratory, and the results will be reported in due course.

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(16) For recent synthesis of **19**, see: Inoue, T.; Kuwajima, I. *J. Chem. Soc., Chem. Commun.* **1980**, 251 and references cited therein and ref 3b.

(17) Synthetic sample showed $[\alpha]^{23}_D$ +49.1° (c 0.5, H_2O) [lit. $[\alpha]^{22.5}_D$ +49.9° (c 1, H_2O)] and satisfactory combustion data of **19** was also obtained.[9] For the optical rotation, see: Nakagawa, Y.; Kanō, H.; Tsukuda, H.; Koyama, H. *Tetrahedron Lett.* **1967**, 4105.

(18) Walton, E.; Holly, F. W.; Boxer, G. E.; Nutt, R. F.; Jenkins, S. R. *J. Med. Chem.* **1965**, *8*, 659.

(19) Compounds of the epoxy series were found unstable to acidic conditions, resulting in easy cleavage.

(20) The corresponding saturated meso compound derived from furan maleic anhydride was hydrolyzed very slowly with the esterase. For the Diels–Alder adduct, see: Daniels, R.; Fischer, J. L. *J. Org. Chem.* **1963**, *28*, 320.

A New Bridging Ligand, the Hydrogen Oxide Ion ($H_3O_2^-$)

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The hydrated hydroxide has been the subject of many investigations,[1-3] but unlike the hydrated proton, structural data on this unit is scarce and limited. Although the existence of species like $H_3O_2^-$, $H_6O_4^{2-}$, $H_7O_4^-$ etc., was proposed on the basis of spectroscopic results,[1,2] it was only recently that the isolation and structural characterization of the first hydroxide hydrate was reported.[4] The X-ray structure analysis in that work showed the existence of a very short and symmetric hydrogen bond in the hydrogen oxide ion, $H_3O_2^-$. This anion was found to lie on a crystallographic inversion center with an O–O distance of 2.29 (2) Å and linked through hydrogen bonds to four adjacent water molecules. The participation of bridging $H_3O_2^-$ ligands in transition states of some redox reactions was proposed by Dodson et al.[5] There have been no reports of the isolation or structural characterization of stable species containing this ligand.

We wish to report the preparation and X-ray structure determination results of the first transition-metal complex containing $H_3O_2^-$ as a bridging ligand between two metal atoms.

Recently we have reported the synthesis and structure of a new class of metal atom cluster compounds having the general formula $[M_3(\mu_3\text{-}X)_2(O_2CR)_6L_3]^{n\pm}$ (M = Mo, W; X = O, CCH_3; L = H_2O, O_2CR).[6] One such W(IV) compound $[W_3O_2(O_2CC_2H_5)_6(H_2O)_3](BF_4)_2\cdot 5.5H_2O$ was crystallized by elution of the cationic cluster from an ion-exchange column with HBF_4 and slow evaporation of the eluant.[6a] It was shown that the triangular 2+ cation possessed a nearly D_{3h} symmetry with average W–W distance of 2.745 (3) Å and average W–O(H_2O) distance of 2.09 (2) Å. We have found now that if HBr or KBr are used for the elution of this ion or its molybdenum analogue[7] from the ion-exchange column, a new class of compounds are obtained. We describe here three compounds, all having the general formula $[M_3O_2(O_2CC_2H_5)_6(H_2O)_2\text{-}(H_3O_2)\text{-}M_3O_2(O_2CC_2H_5)_6(H_2O)_2]$-

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(7) $[Mo_3O_2(O_2CC_2H_5)_6(H_2O)_3]^{2+}$ is obtained by refluxing $Mo(CO)_6$ in a propionic acid/propionic anhydride mixture for 24 h and diluting the solution with H_2O.

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Table I. Structural Data for $\{[M_3O_2(O_2CC_2H_5)_6(H_2O)_2]_2(H_3O_2)\}Br_3 \cdot 6H_2O$

compd	M	bond distances, Å[a]					
		M(1)-M(2)	M(1)-M(3)	M(2)-M(3)	$M-O(H_2O)$	$M-O(H_3O_2^-)$	$O-O(H_3O_2^-)$
1	W	2.743 (1)	2.765 (1)	2.760 (1)	2.11 (1)	1.99 (1)	2.48 (1)
2	Mo	2.750 (2)	2.777 (2)	2.773 (1)	2.11 (1)	2.01 (1)	2.52 (1)
3	Mo	2.743 (1)	2.780 (1)	2.770 (1)	2.11 (1)	2.03 (1)	2.44 (1)
		2.751 (1)	2.779 (1)	2.779 (1)	2.11 (1)	2.02 (1)	

[a] Numbers in parentheses are esd's occurring in the last significant figure. Crystallographically distinct but chemically equivalent distances have been averaged.

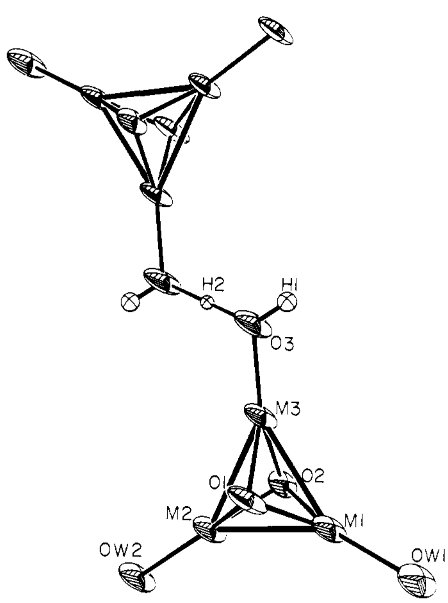

Figure 1. Skeletal structure of $\{[M_3O_2(O_2CC_2H_5)_6(H_2O)_2]_2(H_3O_2)\}^{3+}$ found in compounds **1** and **2**, M = W, Mo. The propionato groups were omitted for the sake of clarity. Hydrogen atoms H(1) and H(2) were located from the difference Fourier transform in compound **2**.

$Br_3 \cdot 6H_2O$ where M = Mo or W.[8] The principal structural results are given in Table I. Compounds **1** and **2** are isostructural and were obtained by elution with 0.5 M KBr. Compounds **2** and **3** are polymorphs; **3** was obtained by the use of 4 M HBr as eluant. The skeletal structure of the above compounds including the bridging $H_3O_2^-$ ligand is depicted in Figure 1. In **1** and **2** there is a crystallographic inversion center midway between the two oxygen atoms of the $H_3O_2^-$ unit while in **3** the asymmetric unit contains an entire $\{[Mo_3O_2(O_2CC_2H_5)_6(H_2O)_2]_2(H_3O_2)\}^{3+}$ ion. The short O-O distance in the bridging group and the presence of one hydroxide anion in the stoichiometry of the complex supports the assignment of $H_3O_2^-$ to this group. As expected the O-O distances in the coordinated $H_3O_2^-$ are longer (by ca. 0.15-0.23 Å) than in the previously reported free $H_3O_2^-$ ion.[4]

From the data in Table I it is obvious that the equilateral metal triangle found in the fluoroborate salt[6a] is subjected in these new bromide salts to considerable distortion. The resulting isosceles triangle is formed by displacement of the bridged metal atom, M(3), toward the $H_3O_2^-$ unit. As a result, the M(3)-M distance [M = M(1) or M(2)] increases by ca. 0.02 Å in **1** and by 0.03 Å in **2** and **3**. The $M(3)-O(H_3O_2^-)$ distance decreases by ca. 0.1 (compared to the average $M-O(H_2O)$ distance of 2.11 Å) to ca. 2.00 Å. A similar decrease of the M-O distance was observed when other negatively charged ligands such as acetate ion replaced a water molecule coordinated to a W(IV) atom in a similar triangular cluster.[6a]

Dodson et al. proposed a mechanism for the isotopic Fe^{2+}/Fe^{3+} exchange reaction based on H-atom transfer via an $H_3O_2^-$ bridge between the iron atoms.[5]

Preliminary results[9] on the base-catalyzed decomposition of the trinuclear cluster $[Mo_3(CCH_3)_2(OAc)_6(H_2O)_3]^{2+}$ in aqueous solution showed that this process is accompanied by an electron transfer from one trimer to another. The axial water molecules in this bulky and inert cluster offer a plausible route for an electron transfer (or H atom transfer) via a bridging $H_3O_2^-$ ligand as found in the stable species reported here.

A series of future papers will provide full reports on the compounds described here and on others that have been discovered. Attempts are made to grow crystals of **1** suitable for neutron diffraction study.

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Supplementary Material Available: Tables of atomic positional parameters for all three compounds (7 pages). Ordering information is given on any current masthead page.

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[8] Compound **1**: $\{[W_3O_2(O_2CC_2H_5)_6(H_2O)_2]_2H_3O_2\}Br_3 \cdot 6H_2O$; space group $P\bar{1}$; $a = 14.320$ (3), $b = 12.101$ (2), $c = 11.417$ (2) Å; $\alpha = 111.13$ (2), $\beta = 105.65$ (2), $\gamma = 66.51$ (2)°; $V = 1674$ (2) Å^3; $Z = 1$; d(calcd) = 2.48, d(obsd) = 2.49 ± 0.01 g cm^{-3}; $R = 0.068$, $R_w = 0.076$. Compound **2**: $\{[Mo_3O_2(O_2CC_2H_5)_6(H_2O)_2]_2H_3O_2\}Br_3 \cdot 6H_2O$; space group $P\bar{1}$; $a = 14.360$ (4), $b = 12.115$ (3), $c = 11.407$ (2) Å; $\alpha = 111.12$ (2), $\beta = 105.75$ (3), $\gamma = 66.65$ (2)°; $V = 1680$ (2) Å^3; $Z = 1$, d(calcd) = 1.95, d(obsd) = 1.96 ± 0.01 g cm^{-3}; $R = 0.055$, $R_w = 0.066$. Compound **3**: $\{[Mo_3O_2(O_2CC_2H_5)_6(H_2O)_2]_2H_3O_2\}Br_3 \cdot 6H_2O$; space group $P\bar{1}$; $a = 18.308$ (5), $b = 15.754$ (4), $c = 11.470$ (3) Å; $\alpha = 98.44$ (2), $\beta = 94.57$ (2), $\gamma = 96.67$ (2)°; $V = 3234$ (2) Å^3; $Z = 2$; d(calcd) = 2.02, d(obsd) = 2.01 ± 0.01 g cm^{-3}; $R = 0.056$, $R_w = 0.069$.

[9] Bino, A.; Gibson, D., unpublished results.

Relationship between Solution Entropies and Gas-Phase Entropies of Nonelectrolytes

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There has been considerable discussion as to the origin of entropies of hydration of gaseous nonelectrolytes. On Pierotti's version of scaled-particle theory (SPT) which yields for solution in water calculated $\Delta S_s°$ values in excellent agreement with experiment,[2] the entire $\Delta S_s°$ term results from the entropy of cavity formation in the solvent,[3] but other workers have suggested that restriction of rotation of flexible molecules is important.[4-6] Wertz[7] has recently put forward the proposition that on hydration all molecules lose a constant fraction of entropy and has argued from this that the $\Delta S_s°$ values arise from loss of internal and (especially) external degrees of freedom of the solute molecules and that there is but little contribution to $\Delta S_s°$ from the solvent itself. It was also suggested by Wertz,[7] though not demonstrated, that a similar proposition would hold for entropies of solution in solvents other than water. In view of the various comments previously made,

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