occupying an axial position. The Ru-S_{ax} bond length of 2.383 (1) Å is substantially longer than the average of the Ru-S_{eq} bond length of 2.207 (10) Å, which is the situation predicted for this diamagnetic low-spin d^4 complex.[17] The Ru-N bond is 2.096 (5) Å in length. The unit cell parameters of $Os(SC_{10}H_{13})_4(CH_3CN)$[18] show it to be isomorphous and presumably isostructural with compound **1**. These compounds are the first examples of five-coordinate ruthenium and osmium complexes in the +4 oxidation state.[19]

In an effort to synthesize ruthenium and osmium compounds with still lower coordination numbers [e.g., $M(SR)_4$, M = Ru, Os], we carried out similar reactions using the more sterically hindered thiolate 2,4,6-triisopropylbenzenethiolate;[21] however, the compounds obtained were $Ru(SC_{15}H_{23})_4(CH_3CN)$ (**3**) and $Os(SC_{15}H_{23})_4(CH_3CN)$ (**4**). As determined by X-ray crystallographic techniques, the arrangement and conformation of the ligands in $Ru(SC_{15}H_{23})_4(CH_3CN)$[22,23] are very similar to those of **1**; the bond distances of the $[RuS_4N]$ core of **1** and **3** are alike, within experimental error.[23] No bonding interactions are apparent between the hydrogens on the orthosubstituents of the ligands and the ruthenium atom. The ruthenium and osmium derivatives of the 2,4,6-triisopropylbenzenethiolate ligands (**3** and **4**) are isomorphous.[24]

In spite of the high oxidation state of the metal and reducing capacity of the thiolate ligands, all four compounds (**1-4**) are thermally and air stable in solution and in the solid state. Other evidence that supports the ability of these thiolate ligands[25] to stabilize high oxidation states of ruthenium and osmium complexes comes from electrochemical measurements. Each of these compounds is the central member of the electron-tranfer series represented by eq 1. The differences between the corresponding

$$[M(SR)_4(L)]^+ \rightleftharpoons [M(SR)_4(L)] \rightleftharpoons [M(SR)_4(L)]^- \quad (1)$$

redox couples[26] of the ruthenium and osmium complexes are small (0.1-0.2 V); a similar situation has been observed for other ruthenium and osmium compounds with sulfur donor ligands.[27]

The new metal-thiolate compounds described in this communication should be good reagents for the syntheses of ruthenium- and osmium-sulfur cluster compounds. Work is continuing.

(16) The bond angles (deg) that define the geometry of the $[RuS_4N]$ core are S1-Ru-N = 178.3 (1), S1-Ru-S2 = 86.36 (6), S1-Ru-S3 = 92.98 (6), S1-Ru-S4 = 89.37 (6), S2-Ru-S3 = 115.89 (7), S3-Ru-S4 = 122.55 (7), S2-Ru-S4 = 121.54 (7).

(17) Rossi, A. R.; Hoffmann, R. *Inorg. Chem.* **1975**, *14*, 365-374 and references therein.

(18) Unit cell parameters for $Os(SC_{10}H_{13})_4(CH_3CN)$ are as follows: monoclinic space group $P2_1/c$ with a = 18.687 (8) Å, b = 11.647 (6) Å, c = 19.225 (5) Å, β = 92.86 (3)°, V = 4179 (3) Å^3, Z = 4.

(19) All other monomeric ruthenium(IV) and osmium(IV) complexes have coordination numbers of six or higher.[20]

(20) Gulliver, D. J.; Levason, W. *Coord. Chem. Rev.* **1982**, *46*, 1-127.

(21) Pearson, D. E.; Caine, D.; Field, L. *J. Org. Chem.* **1960**, *25*, 867-869.

(22) $Ru(SC_{15}H_{23})_4(CH_3CN)$ crystallizes from ethanol in the monoclinic space group $P2_1/n$ with a = 13.844 (3) Å, b = 21.583 (4) Å, c = 22.043 (3) Å, β = 93.90 (2)°, V = 6571 (5) Å^3, Z = 4. Final least-squares refinement gave R = 0.047 and R_w = 0.071 for 5760 reflections with $|F_o| > 3\ \sigma(|F_o|)$.

(23) Bond lengths (Å) and bond angles (deg) of the $[RuS_4N]$ core are Ru-S1 = 2.372 (1), Ru-S2 = 2.207 (1), Ru-S3 = 2.210 (1), Ru-S4 = 2.210 (1), Ru-N = 2.108 (4), S1-Ru-N = 178.1 (1), S1-Ru-S2 = 87.32 (5), S1-Ru-S3 = 93.88 (5), S1-Ru-S4 = 86.96 (4), S2-Ru-S3 = 114.23 (5), S3-Ru-S4 = 121.48 (5), S2-Ru-S4 = 124.25 (5).

(24) Unit cell parameters for $Os(SC_{15}H_{23})_4(CH_3CN)$: monoclinic space group $P2_1/n$ with a = 13.865 (3) Å, b = 21.614 (6) Å, c = 22.034 (6) Å, β = 93.97 (1)°, V = 6587 (5) Å^3, Z = 4.

(25) One of these ligands has been used to prepare a stable iron(III) tetrathiolate complex, $[Fe(SC_{10}H_{13})_4](Et_4N)$.[3]

(26) Polarographic data for the ruthenium and osmium thiolate compounds, $[M(SR)_4(L)]^z$, were obtained in DMF with 0.10 M $(Bu_4N)BF_4$ as the supporting electrolyte and the SCE as the reference electrode. The half-wave potential and slope (in parentheses and as determined by the plot of E vs. log $[(i_d - i)/i]$) for the z = +1/0 and z = 0/-1 couples, respectively, are as follows: +0.68 (57 mV) and -0.85 V (60 mV) for $Ru(SC_{10}H_{13})_4(CH_3CN)$; +0.69 (66 mV) and -0.89 V (61 mV) for $Ru(SC_{15}C_{23})_4(CH_3CN)$; +0.78 (75 mV) and -1.09 V (61 mV) for $Os(SC_{10}H_{13})_4(CH_3CN)$; +0.75 (62 mV) and -1.09 V (60 mV) for $Os(SC_{15}H_{23})_4(CH_3CN)$.

(27) Bond, A. M.; Heath, G. A.; Martin, R. L. *J. Electrochem. Soc.* **1970**, *117*, 1362-1367. Patterson, G. S.; Holm, R. H. *Inorg. Chem.* **1972**, *11*, 2285-2288.

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Registry No. 1, 85479-95-4; **2**, 85479-96-5; **3**, 85506-85-0; **4**, 85479-97-6; $[RuCl_4(CH_3CN)_2](Et_4N)$, 74077-58-0; 2,3,5,6-tetramethylphenyl disulfide, 63157-79-9; 2,4,6-triisopropylphenyl disulfide, 20875-34-7.

Supplementary Material Available: Table of fractional atomic coordinates and thermal parameters and an ORTEP of $Ru(SC_{15}H_{23})_4(CH_3CN)$ (6 pages). Ordering information is given on any current masthead page.

Detection of Hydrogen Bonding in Peptides by the $^{13}C\{^1H\}$ Nuclear Overhauser Effect

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It is well-known that various conformations of peptides and proteins such as α-helix, β-turn, and β-pleated sheets are stabilized by intra- and/or intermolecular hydrogen bonds formed between peptide NH and C=O groups. Several nuclear magnetic resonance (NMR) methods[1] have been employed extensively to characterize such interactions. However, the previous methods, in additon to possibly introducing perturbations into the molecular system,[2] cannot be used to identify a unique hydrogen-bonded pair, i.e., N-H···O=C, simultaneously. Here we present an independent NMR technique that, without disturbing the molecular system, can detect such a hydrogen bonded pair.

The present NMR method is demonstrated on the well-defined model system of valinomycin. It is a cyclic dodecadepsipeptide with a tetramer sequence of L-Val-D-Hyiv-D-Val-L-Lac repeated three times. Various solution conformational models of this molecule in its uncomplexed form have been described.[3,4] The most dominant conformation in nonpolar solvents contains two intramolecular hydrogen bonds, one between the D-Val NH and the L-Lac C=O group and the other between the L-Val NH and the D-Hyiv C=O group, giving a total of six such hydrogen bonds, making the molecule appear like a bracelet.[4] The hydrogen bonding scheme is depicted in Scheme I.

It can be seen from the scheme that each peptide C=O carbon is ^2J coupled to the NH proton of the adjacent amino acid residue (indicated by the broken arrows). In two recent reports[5,6] we made use of this coupling in assigning the ^{13}C and ^1H NMR spectra

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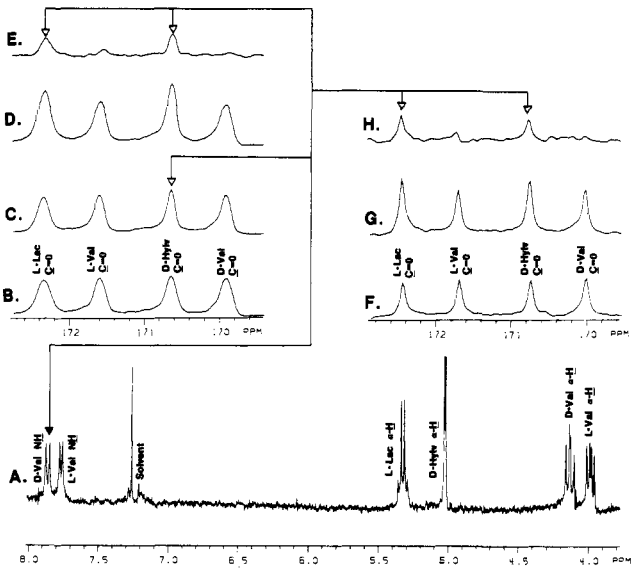

Figure 1. All the experiments were performed on a Nicolet NMC-300 NMR spectrometer. A 35 mM solution of valinomycin was made in deuterated chloroform ($CDCl_3$). The 300-MHz ^1H NMR spectra were obtained by using a 8-μs pulse width for the 90° magnetization vector. All the 75.47-MHz ^{13}C NMR spectra were collected by using a 90° pulse width of 35 μs. Chemical shifts are with respect to Me_4Si as internal standard: (A) ^1H NMR spectrum of valinomycin (NH and α-H proton regions only); (B) carbonyl carbon resonances of valinomycin (coupled without NOE; 800 scans with pulse delay of 30 s; (C) same as B but D·Val NH proton was selectively irradiated without NOE, i.e., during acquisiton; (D) same as B while D·Val NH proton was saturated for NOE only, i.e., before acquisiton; (E) difference spectrum obtained by subtracting B from D, showing the net NOE factors; (F) C=O carbon resonances of valinomycin obtained by the broad-banded decoupling of all the protons but without NOE (64 scans with the pulse delay of 30 s); same as F, with selective irradiation of D·Val NH proton for NOE; (H) difference between F and G. Note that the irradiation of D·Val NH proton is indicated by ▼ while its decoupling effects are shown by ▽.

of peptides and also for sequencing. In order to verify the previous valinomycin assignments,[4] we have selectively decoupled (without NOE) the D·Val NH proton at 7.869 ppm as shown in Figure 1C. Since the D·Hyiv C=O carbon is ^2J coupled to the D·Val NH proton (see the scheme), Figure 1C accordingly shows that the C=O carbon resonance at 170.723 ppm is considerably reduced in its line width. This C=O group therefore belongs to the D-Hyiv residue, which is in exact agreement with the previous results.[4]

The peptide C=O carbon derives part of its nuclear Overhauser enhancement (NOE) from interaction with the adjacent peptide NH proton, which is ^2J coupled as shown above. This observation is given in Figure 1D. Selective irradiation of the D·Val NH proton yields an NOE effect on the D·Hyiv C=O carbon at 170.723 ppm *as well as an additonal NOE effect on the L·Lac C=O carbon at 172.438 ppm* (Figure 1D). The difference spectrum between Figure 1B (coupled) and Figure 1D (selective NOE, irradiation at the D·Val NH proton), shown in Figure 1E, yields the total enhancement factors for the D·Val and L·Lac C=O carbons. This additional NOE for the L·Lac C=O group can be transmitted only through the intramolecular hydrogen bond as shown in the scheme (indicated by the broken arrows).

The experiments described above can also be performed by broad-band decoupling without NOE. An explanation of the technique is given in Figure 1F–H. Figure 1F shows all the C=O carbon resonances obtained by broad-band decoupling without NOE. Figure 1G shows the ^{13}C NMR spectrum of the same carbonyl groups with NOE derived selectively from the D·Val NH proton. The absolute enhancement factors are shown in Figure 1H.

Similarly, NOE effects are observed on the D·Hyiv C=O carbon when the L·Val NH proton is selectively irradiated. The

Scheme I

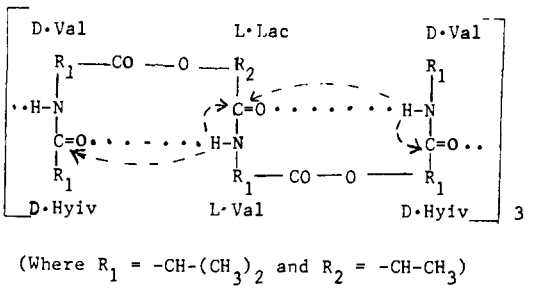

Table I. Fractions of NOE and Internuclear Distances in Valinomycin

proton irradiated	NOE obsd on L·Lac C=O	NOE obsd on D·Hyiv C=O	H bond dist, Å soln	H bond dist, Å cryst[a]
D·Val NH	0.30	0.44	2.22	2.95
L·Val NH	0.43	0.23	2.31	2.95

[a] Values are taken from Karle: Karle, I. *J. Am. Chem. Soc.* 1975, *97*, 4379. Karle also showed two weak H bonds with distances of 3.05 A each. Please see the text for the definition of H bond in solution and crystal.

NOE contribution of the L·Val NH proton to the D·Hyiv C=O carbon, however, is smaller in magnitude than the NOE contribution of the D·Val NH proton to the L·Lac C=O carbon. All the observed NOE fractions thus obtained are listed in Table I. Since the same peptide NH proton is dipolarly coupled to two C=O carbons and since the distance (r) between the NH proton and the C=O carbon atoms belonging to the same peptide moiety is usually known (about 2.08 Å), eq 1[8] below can be used to

$$f(^{13}C_1\{^1H_1\})/f(^{13}C_2\{^1H_1\}) = r_{C_2-H_1}{}^6/r_{C_1-H_1}{}^6 \qquad (1)$$

estimate the hydrogen bond distances. From this equation, with the known bond distance of 2.08 Å, the hydrogen-bond distances are calculated and are also given in Table I. It can be seen in Table I that the calculated hydrogen bond distance of 2.22 Å between the D·Val NH and the L·Lac C=O groups is smaller than in the crystalline form (2.95 Å). However, these values cannot be compared directly. The H-bond distance, as usually defined, particularly in the crystalline form, is between the N atom of NH to the O atom of the C=O group, while in solution the NOE we observed is between the H atom of NH and C atom of the C=O group. The NOE factor is dependent on the distance between these two atoms, which depends on the angle at the O atom of the C=O group. This HOC angle is variable and dependent on the flexibility of the molecule. Although chloroform is a good hydrogen-bond-promoting solvent, conformational flexibilities do occur in solution. The degree of conformational freedom also depends upon the nature of solvents and experimental conditions such as temperature and the nature of hydrogen bonding(s). For example, if it is an intermolecular hydrogen bond, the observation of NOE would greatly depend on the relative strength of the hydrogen bonding, that is, on the efficiency of the cross-relaxation between the hydrogen bonding pairs. In this study, we observed a lower NOE (0.23) between the L·Val NH and the D·Hyiv C=O groups (see Table I). This observation is in agreement with that of Dreele and Stenhouse,[7] who reported that the D·Val NH proton forms a stronger hydrogen bond than that of the L·Val NH proton, although they could not identify the carbonyl group to which a given NH group was hydrogen bonded.

The selective NOE method described in this communication should find wide application in the simultaneous detection of N–H···O=C hydrogen-bonded pairs. In addition, we are currently investigating the extension of the method to molecules with

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complex or partially overlapped spectra by use of 2-D NMR spectroscopy.

Acknowledgment. We are grateful to the UAB Chemistry Department NMR Facility for use of the Nicolet NMC-300 NMR. M.A.K. thanks Drs. C. L. Krumdieck and C. E. Butterworth for their encouragement in this work and acknowledges research support from NIH Grants NS-18350 and CA-Z8103.

Registry No. Valinomycin, 2001-95-8.

Reaction of *cis*-$[Mo(N_2)_2(PMe_3)_4]$ with CO_2. Synthesis and Characterization of Products of Disproportionation and the X-ray Structure of a Tetrametallic Mixed-Valence Mo^{II}–Mo^{V} Carbonate with a Novel Mode of Carbonate Binding

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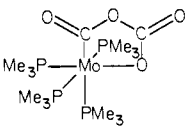
Although most of the emphasis in C_1 chemistry has so far relied on carbon monoxide, the potential application of carbon dioxide as starting material for organic synthesis has been appreciated in recent years.[1] The current interest in CO_2 chemistry and the existence of only a brief report on the reactions of this molecule with dinitrogen complexes of molybdenum[2] prompted us to investigate its interaction with the recently prepared[3] *cis*-$[M(N_2)_2(PMe_3)_4]$ and $[M(N_2)(PMe_3)_5]$ (M = Mo, W) complexes. Here we report preliminary results based on reactions with *cis*-$[Mo(N_2)_2(PMe_3)_4]$ that lead to the formation of a bis-CO_2 complex, $[Mo(CO_2)_2(PMe_3)_4]$ (**1**), two related compounds resulting from the metal-induced disproportionation of CO_2, $[Mo(CO_3)(CO)(PMe_3)_4]$ (**2**), and $[Mo(CO_3)(CO)(PMe_3)_3]_2$ (**3**), and an unusual mixed-valence Mo^{II}–Mo^{V} complex, $[Mo_4(\mu_4\text{-}CO_3)(CO)_2(O)_2(\mu_2\text{-}O)_2(\mu_2\text{-}OH)_4(PMe_3)_6]$ (**4**).

Treatment of petroleum ether solutions of *cis*-$[Mo(N_2)_2(PMe_3)_4]$ (1.1 g, ca. 2.4 mmol, 50 mL) with 50–60 psi of CO_2 at room temperature results in the formation[4] of the pale-yellow **1** and the red-orange **3** in ca. equivalent amounts, together with minor amounts of the dark-blue **2**. Complex **1** can be extracted with toluene from the above mixtures and has a structure still undetermined. Two possibilities can be envisaged: a bis-CO_2 adduct and a head-to-tail dimer $[Mo(C_2O_4)(PMe_3)_4]$. Although efforts to grow crystals suitable for X-ray analysis have so far proved unsuccessful, chemical evidence, particularly the stability of the complex toward loss of CO_2 and the failure to observe CO_2 displacement by N_2, C_2H_4, or phosphine ligands (PMe_3 and PMe_2Ph), seems more in favor of formulation as a head-to-tail dimer A, similar to $[IrCl(C_2O_4)(PMe_3)_3]$.[5]

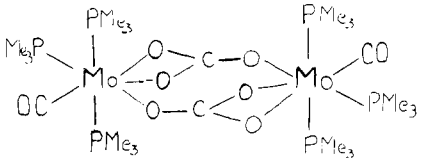


A

Further chemical and spectroscopic studies now in progress may clarify these points. It should be recalled here that although head-to-tail dimers are considered to be intermediates in the metal-induced disproportionation of CO_2, in those instances where they have been isolated, they are stable and do not rearrange.[1a] We have similarly been unable to observe conversion of **1** into the disproportionation products **2** or **3**.

For **2**, formulation as a carbonyl–carbonate complex with a bidentate CO_3 group $[Mo(O_2CO)(CO)(PMe_3)_4]$ comes from both spectroscopic and chemical evidence.[6] Upon attempted dissolution, **2** loses one of the coordinated PMe_3 molecules to afford **3**, which has been characterized by X-ray[7] analysis as a dimeric species with tridentate bridging CO_3 groups, B. Conversely, interaction of **3** with neat PMe_3 yields **2** (eq 1).

$$2[Mo(CO_3)(CO)(PMe_3)_4] \underset{PMe_3}{\overset{THF}{\rightleftharpoons}} [Mo(CO_3)(CO)(PMe_3)_3]_2 \quad (1)$$
2 **3**



B

It is pertinent to note here that the partially characterized complex of composition $[Mo(CO_2)_2(PMe_2Ph)_4]$, formed in the reaction of *cis*-$[Mo(N_2)_2(PMe_2Ph)_4]$ with CO_2 and formulated[2] as a Mo–CO_2 complex, behaves similarly to **2**, dissociating in solution one of the PMe_2Ph ligands to yield $[Mo(CO_3)(CO)(PMe_2Ph)_3]_2$, which is structurally analogous to **3**. Furthermore, the IR data reported for $[Mo(CO_2)_2(PMe_2Ph)_4]$ may also be interpreted[8] by assuming the presence of a carbonyl and a monodentate carbonate ligands, i.e., $[Mo(OCO_2)(CO)(PMe_2Ph)_4]$.

(1) For recent reviews on CO_2 chemistry see: (a) Ibers, J. A. *Chem. Soc. Rev.* **1982**, *11*, 57–73. (b) Floriani, C. *Pure Appl. Chem.*, **1982**, *54*, 59–64. (c) Lapidus, A. L.; Ping, Y. Y. *Russ. Chem. Rev. (Engl. Transl.)* **1981**, *50*, 63–75. (d) Eisenberg, R.; Hendriksen, D. E. *Adv. Catal.* **1979**, *28*, 79–172. (e) Kolomnikov, I. S.; Grigoryan, M. Kh. *Russ. Chem. Rev. (Engl. Transl.)* **1978**, *47*, 334–353. (f) Inoue, S.; Yamazaki, N., Eds. "Organic and Bioorganic Chemistry of Carbon Dioxide"; Wiley: New York, 1982.

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(3) Carmona, E.; Marin, J. M.; Poveda, M. L.; Rogers, R. D.; Atwood, J. L. (a) *J. Organomet. Chem.* **1982**, *238*, C63–C66; (b) *J. Am. Chem. Soc.* in press.

(4) **1**: IR (Nujol) 1685 sh, 1670 vs, 1635 sh, 1155 s, 1135 w, 1100 s (CO_2 groups). Anal. Calcd for $MoC_{14}H_{36}O_4P_4$: C, 34.43; H, 7.38; O, 13.12. Found: C, 34.68; H, 7.57; O, 13.1. **2**: IR 1810 vs (CO), 1600 vs, 1235 m, 1015 w, 840 m (CO_3). Anal. Calcd for $MoC_{14}H_{36}O_4P_4$: C, 34.43; H, 7.38. Found: C, 34.20; H, 7.43. **3**: IR 1765 vs (CO), 1500 vs, 840 m (CO_3). Anal. Calcd for $MoC_{11}H_{27}O_4P_3$: C, 32.04; H, 6.55. Found: C, 32.25; H, 6.75.

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(7) Complex **3** crystallizes in the triclinic space group $P\bar{1}$ with unit cell dimensions a = 9.320 (3) Å, b = 9.570 (3) Å, c 12.010 (4) Å, α = 77.32 (2)°, β = 70.64 (2)°, γ = 64.23 (2), and D_{calcd} = 1.46 g cm^{-3} for Z = 1.

Complex **3** crystallizes in the triclinic space group $P\bar{1}$ with unit cell dimensions a = 9.320 (3) Å, b = 9.570 (3) Å, c 12.010 (4) Å, α = 77.32 (2)°, β = 70.64 (2)°, γ = 64.23 (2), and D_{calcd} = 1.46 g cm^{-3} for Z = 1.

(8) Bands at 1760 (νCO), 1510, and 1335 cm^{-1} (ν_{CO_t} (B_2) and ($\nu_{CO_t} + \nu_{CO_c}$) (A_1), respectively, for monodentate carbonate $(O_t)_2C\text{–}O_c\text{–}M$, assuming linear CO_cM group and C_{2v} symmetry). See: Nakamoto, K. "Infrared and Raman Spectra of Inorganic and Coordination Compounds", 3rd ed.; Wiley: New York, 1978; pp 243–245.

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