in α with electron-withdrawing substituents on the benzene ring (positive p_{xy} coefficient) for the cleavage of benzaldehyde acetals[46,49] and Meisenheimer complexes,[47] and there is evidence for a positive p_{xy} coefficient from α secondary-deuterium-isotope effects in the cleavage of formaldehyde hemiacetals.[55]

The larger change in α with substituents on the alcohol ($p_{xy'}$) than with substituents on the reacting carbon atom (p_{xy}) represents an apparent inconsistency or imbalance of the changes in transition-state structure if these are to be described by a single reaction-coordinate diagram. The imbalance represents a larger movement of the transition state toward the right side of the diagram when the upper left corner is raised than when the top is raised (increased in energy); there is no significant movement to the right when the left edge is raised ($\delta\alpha/\delta pK_{HA} = p_x \simeq 0$). Formally, the imbalance represents a failure of the normalized interaction coefficients to follow the relationship of eq 17. The

$$p_{xy} = p_{xy'} + p_x \qquad (17)$$

same imbalance has been observed previously in the cleavage of carbinolamines and their ethers.[56] The positive p_{xy} coefficients that have been observed for the cleavage of benzaldehyde acetals,[46,49] Meisenheimer complexes,[47] and formaldehyde hemiacetals[55] also show imbalance according to eq 17. There is a similar imbalance between the effects of substituents in the alcohol on the amount of proton transfer ($p_{xy'}$) and the amount of C–O bond cleavage ($p_{y'y'}$) in the transition state for the cleavage of formaldehyde hemiacetals.[55]

These observations indicate that there is a greater tendency for change in the structure of the proton-transfer portion of the transition state, which involves three atoms and two partial bonds, than of the remainder of the transition state, which involves only two heavy atoms and one partial bond. A small part of the imbalance can be accounted for by a simple electrostatic contribution to the $p_{xy'}$ coefficient, but most of it can be explained if there is a net tightening of the transition state for proton transfer as the acid becomes stronger.[56] The imbalance means that the "effective charges" in different parts of the transition state may not be additive; the bond orders for the making and breaking of σ bonds in the different parts of the transition states of these complex reactions also may not be additive to give an integer. The characteristics of these reactions may be easier to understand if they are regarded as an electrophilic attack by the acid on oxygen that withdraws electrons from the C–O bond rather than as C–O cleavage that is assisted by proton transfer.[55]

Acknowledgment. We are grateful to J. Y. Loewenberg and D. Kolodrubetz for carrying out preliminary experiments that demonstrated general-acid catalysis with $\alpha \sim 0.5$ for the methoxyaminolysis of ethyl benzimidate.

Registry No. *m*-NO_2—Ph—C(=NH)OEt, 831-65-2; *p*-NO_2—Ph—C(=NH)OEt, 831-68-5; *p*-Cl—Ph—C(=NH)OEt, 827-72-5; *m*-Cl—Ph—C(=NH)OEt, 827-64-5; *p*-OMe—Ph—C(=NH)OEt, 829-48-1; CH_3ONH_2, 67-62-9; $CF_3CH_2NH_2$, 753-90-2; $CH_3OCH_2CH_2NH_2$, 109-85-3; CH_3NH_2, 74-89-5; $NH_2CONHNH_2$, 57-56-7; $H_2NCOCH_2NH_2$, 598-41-4; $ClCH_2CH_2NH_2$, 689-98-5; ethyl benzimidate, 825-60-5; methoxyethyl benzimidate, 72047-81-5; chloroethyl benzimidate, 72047-82-6; propargyl benzimidate, 41897-10-3; trifluoroethyl benzimidate, 72047-83-7; cyanoacetic acid, 372-09-8; methoxyacetic acid, 625-45-6; acetic acid, 64-19-7; methoxyamine hydrochloride, 593-56-6; cacodylic acid, 75-60-5.

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Communications to the Editor

^{1}H and ^{13}C NMR of Vinylketene and Its Dimerization by [4 + 2] Cycloaddition. Synthesis of Sibirinone and Bicyclo[4.2.1]nona-3,7-dien-2-one

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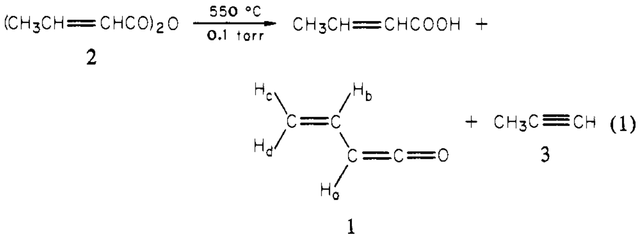
Received May 10, 1982

There have been several reports of the generation of vinylketene (**1**) from various sources.[2] In the earlier work **1** was postulated on the basis of trapping experiments, but recently it has been observed directly by mass,[2f] microwave,[2g,h] and infrared[2g,h] spectroscopy. On the basis of photoelectron spectroscopy and MNDO calculations, the vinylketene structure instead of the ethylideneketene structure was assigned to the product of thermolysis of crotonic acid derivatives.[2j] In this communication we report the low-temperature ^{1}H and ^{13}C NMR spectra of **1** and some chemistry of **1**.

The vacuum pyrolysis (eq 1) of crotonic anhydride[2h,j,3] was carried out by using an apparatus with two product condensers, the first cooled to −20 °C and the second to −196 °C, in order to separate the crotonic acid from the more volatile products.[4] After pyrolysis, a mixture of CS_2 and $CDCl_3$ was distilled into the −196 °C condenser, the mixture was allowed to warm to −78 °C, and a standard was added. The ^{1}H NMR spectrum of the resulting solution at −70 °C showed a 22% yield of **1** [4.0 (H_a, d, J_{ab} = 11 Hz), 4.6 (H_c dd, J_{bc} = 11 Hz, J_{cd} = 1.5 Hz), 4.9 (H_d dd, J_{bd} = 18 Hz, J_{cd} = 1.5 Hz), 5.9 (H_b, ddd, J_{ab} = 11 Hz, J_{bc} = 11 Hz, J_{bd} = 18 Hz)], a 40% yield of methylacetylene[2g–i] (**3**) [1.89 (s, 1), 1.88 (s, 3)], and only 5% of minor products. No evidence for the cyclic isomer of **1**, cyclobutenone,[5] was obtained.



2

1

3

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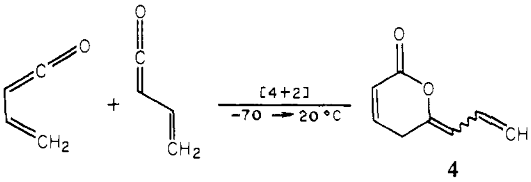
[1] On sabbatical leave from Frostburg State College, Frostburg, MD.
[2] (a) Rousseau, G.; Bloch, R.; LePerchec, P.; Conia, J. M. *J. Chem. Soc., Chem. Commun.* **1973**, 795. (b) Brown, R. F. C.; Eastwood, F. W.; Harrington, K. J. *Aust. J. Chem.* **1974**, *27*, 2373. (c) Holder, R. W.; Freiman, H. S.; Stefanchik, M. F. *J. Org. Chem.* **1976**, *41*, 3303. (d) Ripoll, J. L. *Tetrahedron* **1977**, *33*, 389. (e) Ripoll, J. L.; Rouessac, A.; Rouessac, F. *Tetrahedron* **1978**, *34*, 19. (f) Terlouw, J. K.; Burkers, P. C.; Holmes, J. L. *J. Am. Chem. Soc.* **1979**, *101*, 225. (g) Brown, R. D. Godfrey, P. D.; Woodruff, M. *Aust. J. Chem.* **1979**, *32*, 2103. (h) Bjarnov, E. *Z. Naturforsch., A.* **1979**, *34A*, 1269. (i) Bloch, R.; Orvane, P. *Tetrahedron Lett.* **1981**, *22*, 3597. (j) Mohmand, S.; Hirabayashi, T.; Bock, H. *Chem. Ber.* **1981**, *114*, 2609.
[3] Clover, A. M.; Richmond, G. F. *Am. Chem. J.* **1903**, *29*, 179.
[4] The pyrolysis apparatus and its operating procedure have been described in Trahanovsky, W. S.; Ong, C. C.; Lawson, J. A. *J. Am. Chem. Soc.* **1968**, *90*, 2839.
[5] Sieja, J. B. *J. Am. Chem. Soc.* **1971**, *93*, 2481.

This is consistent with the report that cyclobutenone opens to **1** thermally.[2e] The chemical shift for the ketenic hydrogen (H_a) is about the same as those for the corresponding hydrogens of *cis*- and *trans*-1-propenylketene.[6] The ^{13}C NMR spectrum of the product mixture (−70 °C) also showed **1** [δ 200.2 (s), 121.9 (d, J_{CH} = 155 Hz), 109.1 (dd, J_{CH} = 154, 162 Hz), 28.6 (d, J_{CH} = 173 Hz)],[7] and **3** [δ 80.4 (s), 68.3 (d, J_{CH} = 248 Hz), 3.7 (q, J_{CH} = 132 Hz)]. The IR spectrum of the product mixture at room temperature showed an absorption at 3330 cm^{-1}, further confirming the presence of **3**, which is probably formed by loss of carbon monoxide from **1** followed by rearrangement of the resulting vinyl carbene.[2i,9]

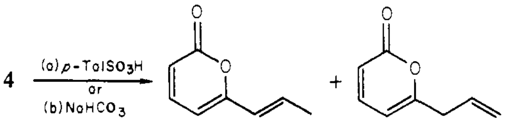
When the product mixture is warmed to room temperature, **1** is converted primarily to **4** (70%), a [4 + 2] cycloaddition dimer of **1** (eq 2). Although **4** is difficult to purify, the structure was evident from spectra of the crude material.[10] Other vinylketenes have been shown to react as dienes in [4 + 2] cycloadditions,[11] and there are examples of the ketene carbonyl group reacting as a dienophile,[12] but we are aware of no other vinylketene that acts as both in dimerization. The closely related isopropenylketene gave a β-lactone dimer,[13] a reaction more typical of aldoketenes.[14]



4

(70%) (2)

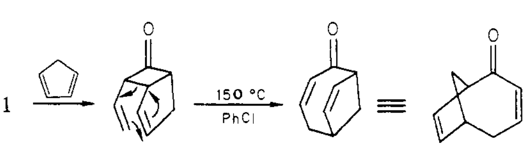
The structure of **4** was confirmed by isomerization to α-pyrones **5** and **6** (eq 3). Acid-catalyzed isomerization yields primarily **5**[10] (50%), which is sibirinone,[15,16] a recently discovered metabolite of *Hypomyces semitranslucens* G. Arnold. If isomerization of **4** is effected by base, a 1:3 mixture of **5** and 6-allyl-α-pyrone (**6**)[10] is obtained (50–60%).[17]



5 6

(3)

(a) 9:1
(b) 1:3

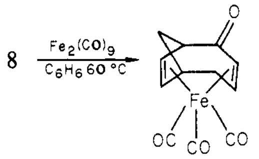


7 8 8

(4)

When **1** is prepared this way and cyclopentadiene is added to the condenser before warming (eq 4), *endo*-7-vinylbicyclo[3.2.0]hept-2-en-6-one (**7**)[10] is obtained (23% based on anhydride).[18] The structure of **7**, the expected structure based on previous studies of ketene cycloadditions,[2c,19] is indicated by its spectral properties and its facile isomerization to bicyclo[4.2.1]nona-3,7-dien-2-one (**8**)[10] (40%). The low yield of **8** is due to a retro-[2 + 2] cycloaddition of **7** as evidenced by the presence of cyclopentadiene and **6** in the product mixture. Compound **8** is a novel bicyclo[4.2.1]nonadienone and may serve as a precursor of other bicyclo[4.2.1]nonanes,[20] a class of compounds that has received considerable attention recently.[22] The [2 + 2] cycloaddition followed by a Cope rearrangement constitutes a formal [4 + 4] cycloaddition and may find further use as a synthetic strategy. This might be the mode of reaction in the homobullvalenone rearrangement postulated to occur via a [4 + 4] cycloaddition of a vinylketene intermediate.[23]

Dienone **8** was converted (eq 5) to (3,4,7,8-η^4-bicyclo[4.2.1]nona-3,7-dien-2-one)tricarbonyliron (**9**)[10] (13%). Inspection of a Dreiding model of **8** indicates that there are two low-energy conformations: one that corresponds to that shown in **9** and one in which the seven-membered ring is in the boat conformation. There is evidence that the related compound, bicyclo[4.2.1]non-3-en-2-one, prefers the latter.[22a]



9

(5)

Acknowledgment. This research was supported in part by a grant from the donors of the Petroleum Research Fund, administered by the American Chemical Society. Funds from the National Science Foundation were used to purchase the Finnigan Model No. 4023-000 gas chromatograph–mass spectrometer data system.

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(6) Schiess, P.; Radimerski, P. *Helv. Chim. Acta* **1974**, *57*, 2583.

(7) The ketene moiety is revealed by the signals at δ 200.2 and 28.6.[8]

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(10) All new compounds were fully characterized by ^{1}H and ^{13}C NMR and IR spectroscopy and, if stable enough, by mass spectroscopy and/or an exact mass. Physical properties are recorded in the supplementary material.

(11) (a) Mayr, H. *Angew. Chem.* **1975**, *87*, 491. (b) Kuzuya, M.; Miyake, F.; Okada, T. *Tetrahedron Lett.* **1980**, *21*, 1043. (c) Danheiser, R. L.; Sard, H. *J. Org. Chem.* **1980**, *45*, 4810. (d) Day, A. C.; McDonald, A. N.; Anderson, B. F.; Bartczak, T. J.; Hodder, O. J. R. *J. Chem. Soc., Chem. Commun.* **1973**, 247.

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(15) Nair, M. S. R.; Carey, S. T. *Phytochemistry* **1977**, *16*, 1613.

(16) In ref 15 the *m/e* value of the (M − CO − CHO) peak should be 79 instead of 89.

(17) In a related synthesis of 2-pyrones from α,β-unsaturated acid chlorides and tertiary amines, crotonyl chloride failed to yield the expected mixture of **5** and **6**: Rey, M.; Dunkelblum, E.; Allain, R.; Dreiding, A. S. *Helv. Chim. Acta* **1970**, *53*, 2159.

(18) Compound **7** has also been formed by in situ generation of vinylketene from crotonyl chloride and triethylamine in the presence of cyclopentadiene but was isomerized in the basic medium to a pair of conjugated cyclobutanone cis–trans isomers.[2c]

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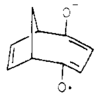
(20) Professor Glen A. Russell and T. Morita have converted **8** to i by oxidizing with O_2 in Me_2SO containing *t*-BuOK.[21]



i

(21) Russell, G. A.; Morita, T., unpublished work.

(22) (a) Boerth, D. W.; Van-Catledge, F. A. *J. Org. Chem.* **1975**, *40*, 3319. (b) Sadlo, H.; Kraus, W. *Tetrahedron* **1978**, *34*, 1965. (c) Gillissen, H. M. J.; Schipper, P.; Buck, H. M. *Recl. Trav. Chim. Pays-Bas* **1980**, *99*, 346. (d) Dyllick-Brenzinger, R.; Olsen, H. *J. Am. Chem. Soc.* **1981**, *103*, 704. (e) Ruechardt, C.; Golzke, V.; Range, G. *Chem. Ber.* **1981**, *114*, 2769.

(23) Goldstein, M. J.; Dai, S.-H. *J. Am. Chem. Soc.* **1973**, *95*, 933.

(24) **Note Added in Proof**: The synthesis of substituted bicyclo[4.2.1]nonadienones via substituted vinylketenes generated in solution has been reported: Huston, R.; Rey, M.; Dreiding, A. S. *Helv. Chim. Acta* **1982**, *65*, 451. The unsubstituted compounds, vinylketene (**1**) and bicyclo[4.2.1]nona-3,7-dien-2-one (**8**), were not included in this study.

Registry No. 1, 50888-73-8; **2**, 623-68-7; **3**, 74-99-7; **4**, 82554-87-8; **5**, 64767-86-8; **6**, 82554-88-9; **7**, 81496-45-9; **8**, 82554-89-0; **9**, 82544-81-8; cyclopentadiene, 542-92-7.

Supplementary Material Available: Listing of physical properties of compounds **4**–**9** (3 pages). Ordering information is given on any current masthead page.

Preparation and Characterization of a Compound Containing the Octachloroditungstate ($W\overset{4}{—}W$) Ion, $[W_2Cl_8]^{4-}$

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Rapid development of the chemistry of the quadruply bonded Mo_2^{4+} unit[1] has not been followed by comparable progress in the chemistry of the isoelectronic W_2^{4+} unit. The reasons for this lack of close homology have only recently begun to emerge[2] and have interesting implications in the broader understanding of transition-metal chemistry. While the chemistry of W_2^{4+} has not been totally lacking and there are even a few classes of compounds, such as the $W_2(2\text{-oxopyridine})_4$[3] and $W_2Cl_4(PR_3)_4$[4] types, with stability comparable to that of their molybdenum analogues, the truly prototypal species $W_2(O_2CR)_4$ and $[W_2Cl_8]^{4-}$ have been extraordinarily elusive. Methods for preparing compounds of the former type have recently been found,[5] but until now, no compound containing the simple $[W_2Cl_8]^{4-}$ ion has been proven to exist.[6,7] That lacuna has now been filled.

During the preparation[4a] of the $W_2Cl_4(PR_3)_4$ compounds by the Na/Hg reduction of $(WCl_4)_x$ in THF in the presence of PR_3, it was noticed that in the absence of PR_3 a one-electron reduction of $(WCl_4)_x$ yielded $W_2Cl_6(THF)_4$, and a subsequent one-electron reduction (per W) of isolated $W_2Cl_6(THF)_4$ yielded an intense blue solution. We have now been able to isolate a blue powder from this solution that has the composition $Na_4(THF)_xW_2Cl_8$ (x is variable, usually 2–4).[8,9] A THF solution of $Na_4W_2Cl_8$ begins to deposit a black precipitate after a few minutes at 25 °C, and the solution eventually becomes colorless. At -20 °C the visible spectrum of a THF solution of $Na_4W_2Cl_8$ shows a peak at 600 nm with an ϵ of ~1600, consistent with this compound being a sodium salt of $[W_2Cl_8]^{4-}$.[10,11]

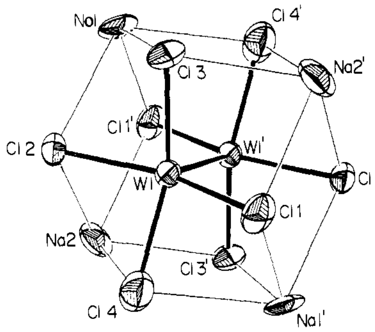

Figure 1. One of the two $[W_2Cl_8]^{4-}(Na^+)_4$ groups in the crystal of $Na_4(TMEDA)_4W_2Cl_8$ This one resides at the unit cell origin while the other, which is substantially identical, resides at the unit cell center. An inversion center lies at the midpoint of the $W\overset{4}{—}W$ bond. Each atom is represented by its ellipsoid of thermal vibration scaled to enclose 30% of the electron density.

Table I. Dimensions of the $[W_2Cl_8]^{4-}$ Ions

	Distances (Å)		
W(1)–W(1)′	2.259 (1)[a]	W(2)–Cl(5)	2.417 (3)
W(2)–W(2)′	2.254 (1)	–Cl(6)	2.437 (3)
mean W–W	2.257 [3][a]	–Cl(7)	2.426 (3)
		–Cl(8)	2.446 (3)
W(1)–Cl(1)	2.426 (3)	mean W–Cl	2.429 [5]
–Cl(2)	2.421 (3)		
–Cl(3)	2.450 (4)		
–Cl(4)	2.412 (4)		
	Angles (deg)		
W(1)′–W(1)–Cl(1)	103.58 (9)	W(2)′–W(2)–Cl(5)	104.27 (9)
–Cl(2)	103.12 (9)	–Cl(6)	103.6 (1)
–Cl(3)	103.6 (1)	–Cl(7)	103.70 (9)
–Cl(4)	103.9 (1)	–Cl(8)	103.13 (9)
		mean W–W–Cl	103.5 [1]

[a] A number in parentheses is the estimated standard deviation of that individual value. A number in brackets is equal to $[\Sigma_n \Delta_i^2 / n(n-1)]^{1/2}$, where Δ_i is the deviation of the ith value in a set of n such values from the arithmetic mean.

Initial attempts to isolate crystalline compounds containing the $[W_2Cl_8]^{4-}$ ion revealed that both thermal instability and sensitivity to oxidants (including coordinated solvents) posed problems. However, crystals of a tetramethylethylenediamine (TMEDA) derivative can be prepared ~50% of the time in the following manner. After the mixture of $Na_4W_2Cl_8$ and black decomposition product[8] is extracted with a minimal amount of cold THF, approximately 5 equiv of TMEDA are added, and the solution is cooled to ~−30 °C. After 1 day blue crystals have formed, usually mixed with some green microcrystalline decomposition product.

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[3] Cotton, F. A.; Fanwick, P. E.; Niswander, R. H.; Sekutowski, J. C. *J. Am. Chem. Soc.* **1978**, *100*, 4725.

[4] (a) Sharp, P. R.; Schrock, R. R. *J. Am. Chem. Soc.* **1980**, *102*, 1430. (b) Cotton, F. A.; Felthouse, T. R.; Lay, D. G. *Ibid.* **1980**, *102*, 1431.

[5] Sattelberger, A. P.; McLaughlin, K. W.; Huffman, J. C. *J. Am. Chem. Soc.* **1981**, *103*, 2880.

[6] An SCF-Xα-SW calculation[7] in 1977 on the $[W_2Cl_8]^{4-}$ ion (with an estimated W–W distance of 2.20 Å) led to the following conclusions: (1) There is "no indication that this ion should be incapable of existence or even particularly unstable". (2) Relative to $[Mo_2Cl_8]^{4-}$ and $[Re_2Cl_8]^{2-}$, "the destabilization of the δ orbital in $[W_2Cl_8]^{4-}$ should lead to oxidation or oxidative addition reactions involving the quadruple bond. This would account for ... the ... small number of W–W quadruply bonded systems" isolated up to that time. This was the first statement of the now accepted view as to why quadruply bonded W_2^{4+} compounds are frequently less stable[2] than their molybdenum analogues, and it provides the basis for designing synthetic procedures such as the present one that allow the isolation of such compounds.

[7] Cotton, F. A.; Kalbacher, B. J. *Inorg. Chem.* **1977**, *16*, 2386.

[8] Filtration of the intense blue solution through Celite followed by removal of the THF in vacuo leaves a blue powder mixed with an insoluble, finely divided black material. Extraction with minimal THF followed by filtration and removal of the THF in vacuo yields a blue powder that is virtually free of the black material. After the sample was pumped on at ~0.1 mmHg for 1 h, it had the approximate composition $Na_4(THF)_2W_2Cl_8$.[9a] Another sample exposed to a high vacuum (<1 μmHg) at 25 °C overnight had the approximate composition $Na_4(THF)W_2Cl_8$.[9b] We believe that the maximum possible equivalents of THF is 8 (i.e., $Na_4(THF)_8W_2Cl_8$; cf. $Na_4(TMEDA)_4W_2Cl_8$). The yield of $Na_4(THF)_xW_2Cl_8$ is limited because of the deficiency of chloride, but if one assumes that $2W_2Cl_6 + 2Na \rightarrow 0.5Na_4W_2Cl_8 + 2\text{"}WCl_2\text{"}$, then the yields are close to the theoretical 50%.

[9] (a) Anal. Calcd for $WC_4H_8Cl_4Na_2O$: C, 10.83; H, 1.82; Cl, 31.96. Found: C, 9.03; H, 1.57; Cl, 31.06. (b) Anal. Calcd for $WC_2H_4Cl_4Na_2O_{0.5}$: C, 5.89; H, 0.98; Cl, 34.78; Na, 11.28. Found: C, 4.96; H, 0.84; Cl, 33.83; Na, 11.80.

[10] The peak position is consistent with that for $[Mo_2Cl_8]^{4-}$ of ca. 480 nm in view of the correlation of Sattelberger and Fackler[11] for the series of $[M_2(CH_3)_8]^{4-}$ ions.

[11] Sattelberger, A. P.; Fackler, J. P. *J. Am. Chem. Soc.* **1977**, *99*, 1258.

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