3172 *Inorg. Chem.* **1980**, *19*, 3172–3175

Notes

Contribution from the Department of Chemistry,
University of Wisconsin—Madison, Madison, Wisconsin 53706

Preparation and Structure of a Reduced-State Zirconium Cluster Containing Triangular $[Zr_3Cl_6]^{n+}$ Units

James Kleppinger, Julie Wrazel, Joseph C. Calabrese, and Edwin M. Larsen*

Received July 19, 1979

The number of known zirconium cluster species is small. Besides $Zr_{12}Al_4Cl_{51}$,[1] which is more explicitly detailed here, the other characterized zirconium cluster species are $[Zr_6Cl_{12}]Cl_{6/2}$[2] and $[Zr_6I_6]I_{12/2}$.[2] It is likely that $[(Me_6C_6)_3Zr_3Cl_6]Cl$[3] is also a cluster with a structure similar to that of the chloro-bridged trinuclear niobium[4] analogue. In the species described here the zirconium atoms are in trigonal-prismatic coordination, which, although known in several layer compounds such as ZrS_3,[5] $ZrSe_3$,[5] $ZrTe_3$,[5] and $ZrCl_2$,[6,7] is relatively uncommon for zirconium compounds.

Experimental Section

The handling techniques and reagents used are identical with those previously described[8] except that reactor grade $ZrCl_4$ (Alfa Inorganics, 61-ppm Hf) and zirconium metal (Wah Chang, 180-ppm Hf) were used in the reaction. The product is isolated from the same $ZrCl_4$–Al_2Cl_6–Zr reaction system[8] from which crystalline zirconium(III) chloride is isolated except that the temperature is 200 ± 10 °C rather than 230 ± 10 °C. The cluster is deposited from the blue homogeneous solution as blue-black crystals at the lip of the melt which are recovered by subliming the volatile components of the melt to the lower end of the ampule away from the crystals. The yield is about 250 mg/run, but the reaction mixture can be recycled and a new batch of crystals grown.

The crystals cleave easily at a small angle to the plane normal to the needle axis and powder readily to form a green powder. Chemically, the properties of the cluster parallel those of zirconium(III) chloride.[8] It is oxidized by water and oxygen and is insoluble in liquid aluminum chloride except in the presence of zirconium(IV) chloride where it dissolves to yield the same blue solution from which it was deposited.

The crystals were analyzed for zirconium, aluminum, and chlorine. Chloride was determined gravimetrically. Approximately 100 mg of the crystals was dissolved in 15 mL of distilled deionized water to which 15 mL of acetone was added after a transient orange color had dissipated. Silver chloride was precipitated by the dropwise addition of ~0.10 M $AgNO_3$ in 50% H_2O/acetone and weighed in porcelain filtering crucibles. Sodium chloride analyzed under these conditions gave 60.63 ± 0.08% compared to the theoretical 60.66%. Zirconium and aluminum were analyzed by atomic absorption spectroscopy. A matrix containing 5% HCl and 2% F^- (as NH_4F) in distilled and deionized water was used in the analyses. The high chloride concentration was used to swamp out the enhancing effects of chloride on the signals of both metals, and fluoride ion was added to prevent the formation of hydroxylated polymeric metal species. In the zirconium analysis, approximately 250 mg of crystals was dissolved in 500 mL of the matrix. As the zirconium solutions were found to be very sensitive to dilution losses, they were analyzed by a standard additions technique. A series of solutions of known zirconium content in which the aluminum concentration was held constant and approximately equal to that of the unknown solution was used. The accuracy of the zirconium analysis by atomic absorption was limited by the refractory nature of the metal which resulted in an exceptionally noisy flame. Samples of zirconium metal analyzed by this technique gave an average recovery rate of 98 ± 3%. In the analysis of aluminum, approximately 100 mg of sample was dissolved in 500 mL of the matrix. This solution was bracketed by solutions of known aluminum content in which the ratio of zirconium to aluminum by weight was held constant and approximately equal to that in the crystals.

The analytical data on a total of 29 different preparations gave Zr = 36.52 ± 0.59% (12 analyses), Al = 3.61 ± 0.14% (nine analyses), and Cl = 59.97 ± 0.30% (eight analyses), for a total of 100.0 ± 0.68% which corresponds to a calculated composition of $Zr_{12}Al_{4.01}Cl_{50.7}$. A FORTRAN IV program developed by Miller et al.[9] was used to fit the experimentally determined analytical data to possible formulations. The formula which best fit the data had the composition $Zr_{12}Al_4Cl_{51}$ and a formal zirconium oxidation-state distribution of nine zirconium(III) and three zirconium(IV) atoms.

Far infrared spectra were recorded as Nujol mulls on a Digilab FTS-20 Fourier transform infrared spectrometer over the range 600–100 cm^{-1}. The mulls were made in the drybox, spread between polyethylene plates of the cell, transported in nitrogen-filled screw-cap bottles, and mounted in the spectrometer under a flow of nitrogen.

The magnetic susceptibility of this compound was determined[10] on a suitably encapsulated sample by the Faraday method over the temperature range of 5–300 K.

The density of the crystals determined by the flotation method was 2.62 g/cm^3 compared to the calculated X-ray density of 2.54 g/cm^3.

X-ray data were obtained on two different crystals. The first crystal, with a length of 2 mm and an average diameter of 0.07 mm, was mounted under dry nitrogen in a Lindemann glass capillary and held in place with a small glass rod. Crystal alignment, space group determination, and data gathering were all carried out on a Syntex $P\bar{1}$ diffractometer using Mo Kα radiation. The space group was determined as monoclinic $I2/m$ (nonstandard for convenience) with cell constants a = 22.216 (3) Å, b = 13.323 (4) Å, c = 6.6236 (7) Å, β = 90.150 (11)°, and V = 1960.44 (63) Å^3. Data were taken I centered ($h + k + l = 2n + 1$ omitted) for $^1/_4$ of the sphere (hkl, $\bar{h}kl$) from $3° \leq 2\theta \leq 45°$ by using a variable scan rate of 2–24 °/min with a background to scan time ratio of 0.67. The intensities of two standard reflections monitored periodically throughout the data collection indicated the stability of the intensities. The data, corrected for Lorentz–polarization effects, yielded 1190 independent reflections with $I > 2\sigma(I)$. The data were consistent with Im, $I2$, or $I2/m$ as potential space groups. The structure, solved from a Patterson map, was further verified by Fourier maps using $I2$ or Im symmetry. In all cases, centrosymmetrically related electron density peaks were generated in these symmetries. Least-squares refinement on two independent zirconium and six independent chorine atoms corrected for anomalous dispersion gave values of R_1 = 11.90, R_2 = 19.16, and error of fit = 5.33.

A second crystal, 0.65 mm in length with an average diameter of 0.23 mm, was loaded as before. The preliminary Syntex routines confirmed the Laue symmetry $I2/m$. The cell parameters were

---

[1] Presented at the 170th National Meeting of the American Chemical Society, Chicago, IL, August 1975; based in part upon a dissertation submitted by James Kleppinger to the Graduate School of the University of Wisconsin, Madison, WI, in partial fulfillment of the requirements for the Ph.D. degree, 1975.

[2] Corbett, J. D.; Daake, R. L.; Poppelmeier, K. R.; Guthrie, D. H. *J. Am. Chem. Soc.* **1978**, *100*, 652–654.

[3] Fischer, E. O.; Röhrschied, F. *J. Organomet. Chem.* **1966**, *6*, 53–66.

[4] Churchill, M. R.; Chang, S. W.-Y. *J. Chem. Soc., Chem. Commun.* **1974**, 248–249.

[5] Brattas, L; Kjekhus, A. *Acta Chem. Scand.* **1972**, *26*, 3441–3449.

[6] Troyanov, S. I.; Tsirel'nikov, V. I. *Moscow Univ. Chem. Bull. (Engl. Transl.)* **1973**, *28*, 44–47.

[7] Cisar, A.; Corbett, J. D.; Daake, R. L. *Inorg. Chem.* **1979**, *18*, 836–843.

[8] Larsen, E. M.; Moyer, J.; Camp, M. J.; Gil-Arnao, F. *Inorg. Chem.* **1974**, *13*, 574–581.

[9] Miller, J. S., personal communication, 1978.

[10] Feldmann, C. D. Ph.D. Thesis, University of Wisconsin—Madison, Madison, WI, 1979.

0020-1669/80/1319-3172$01.00/0

Table I. Interatomic Distances (Å) and Angles (Deg) for $Zr_{12}Al_4Cl_{51}$ (Monoclinic Data)

Interatomic Distances

Zr(1)–Zr(1)^a	3.916 (6)	Zr(2)–Cl(6)	2.521 (10)
Zr(1)–Zr(2)	3.354 (3)	Zr(2)–Cl(6)^C	2.496 (10)
Zr(1)–Cl(1)	2.544 (9)	Cl(1)–Cl(1)^B	3.628 (17)
Zr(1)–Cl(1)′	2.545 (9)	Cl(2)–Cl(1)	3.330 (9)
Zr(1)–Cl(2)	2.489 (7)	Cl(2)–Cl(2)	3.327 (13)
Zr(1)–Cl(3)	2.498 (7)	Cl(2)–Cl(3)	3.225 (9)
Zr(1)–Cl(4)	4.141 (9)	Cl(2)–Cl(4)	3.330 (10)
Zr(1)–Cl(5)	4.142 (10)	Cl(2)–Cl(6)^C	3.365 (12)
Zr(2)–Zr(2)	3.408 (5)	Cl(3)–Cl(1)^a	3.326 (10)
Zr(2)–Zr(2)^a	3.769 (5)	Cl(3)–Cl(3)′	3.321 (14)
Zr(2)–Cl(2)	2.539 (6)	Cl(3)–Cl(6)	3.354 (13)
Zr(2)–Cl(2)′	4.217 (7)	Cl(5)–Cl(3)	3.333 (11)
Zr(2)–Cl(3)	2.544 (7)	Cl(5)–Cl(4)	3.236 (13)
Zr(2)–Cl(3)′	4.218 (7)	Cl(5)–Cl(6)	3.352 (12)
Zr(2)–Cl(4)	2.529 (7)	Cl(6)–Cl(6)^C	3.312 (22)
Zr(2)–Cl(5)	2.520 (7)		

Interatomic Angles

Zr(2)–Zr(1)–Zr(2)′	61.06 (9)	Zr(1)–Zr(2)–Zr(2)′	59.47 (5)
Zr(2)–Zr(1)–Cl(1)	131.6 (2)	Zr(1)–Zr(2)–Cl(2)	47.5 (2)
Zr(2)–Zr(1)–Cl(1)^B	131.4 (2)	Zr(1)–Zr(2)–Cl(3)	47.7 (2)
Zr(2)–Zr(1)–Cl(2)	48.8 (2)	Zr(1)–Zr(2)–Cl(4)	88.3 (2)
Zr(2)–Zr(1)–Cl(2)′	91.2 (2)	Zr(1)–Zr(2)–Cl(5)	88.5 (2)
Zr(2)–Zr(1)–Cl(3)	48.9 (2)	Zr(1)–Zr(2)–Cl(6)	130.6 (3)
Zr(2)–Zr(1)–Cl(3)′	91.0 (2)	Zr(1)–Zr(2)–Cl(6)^C	131.4 (3)
Cl(1)–Zr(1)–Cl(1)^B	79.4 (3)	Zr(2)′–Zr(2)–Cl(2)	89.1 (2)
Cl(2)–Zr(1)–Cl(1)	82.8 (2)	Zr(2)′–Zr(2)–Cl(3)	89.0 (2)
Cl(2)–Zr(1)–Cl(1)^B	134.3 (2)	Zr(2)′–Zr(2)–Cl(4)	47.6 (1)
Cl(2)–Zr(1)–Cl(2)′	83.9 (3)	Zr(2)′–Zr(2)–Cl(5)	47.5 (2)
Cl(2)–Zr(1)–Cl(3)	80.6 (2)	Zr(2)′–Zr(2)–Cl(6)	130.8 (3)
Cl(2)–Zr(1)–Cl(3)′	136.4 (2)	Zr(2)′–Zr(2)–Cl(6)^C	130.1 (3)
Cl(3)–Zr(1)–Cl(1)	134.3 (2)	Cl(5)–Zr(2)–Cl(2)	132.7 (2)
Cl(3)–Zr(1)–Cl(1)^B	82.5 (2)	Cl(5)–Zr(2)–Cl(3)	82.3 (3)
Cl(3)–Zr(1)–Cl(3)′	83.3 (3)	Cl(5)–Zr(2)–Cl(4)	79.7 (3)
Cl(2)–Zr(2)–Cl(3)	78.7 (2)	Cl(5)–Zr(2)–Cl(6)	83.3 (3)
Cl(2)–Zr(2)–Cl(4)	82.1 (3)	Cl(5)–Zr(2)–Cl(6)^C	135.5 (4)
Cl(2)–Zr(2)–Cl(6)	135.6 (4)	Zr(1)–Cl(1)–Zr(1)^a	100.6 (3)
Cl(2)–Zr(2)–Cl(6)^C	83.9 (3)	Zr(1)–Cl(2)–Zr(2)	83.7 (2)
Cl(3)–Zr(2)–Cl(6)	82.9 (4)	Zr(1)–Cl(3)–Zr(2)	83.4 (2)
Cl(3)–Zr(2)–Cl(6)^C	136.9 (4)	Zr(2)–Cl(4)–Zr(2)′	84.7 (3)
Cl(6)–Zr(2)–Cl(6)^C	82.6 (4)	Zr(2)–Cl(3)–Zr(2)′	85.1 (3)
Cl(4)–Zr(2)–Cl(3)	132.7 (2)	Zr(2)–Cl(6)–Zr(2)^a	97.4 (4)
Cl(4)–Zr(2)–Cl(6)	136.9 (4)		
Cl(4)–Zr(2)–Cl(6)^C	82.4 (4)		

[a] Intertriangular distances and angles.

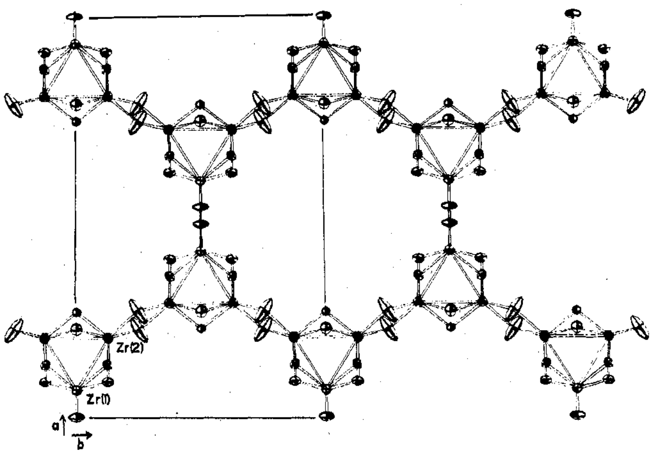


Figure 1. Structure of the Zr–Cl backbone, viewed along the c axis, showing the hole formed by the chloro-bridged zirconium atom triangles.

redetermined as $a = 22.223$ (4) Å, $b = 13.323$ (3) Å, $c = 6.6227$ (11) Å, $\beta = 90.146$ (13)°, and $V = 1962.34$ Å^3. Data were taken for a primitive unit cell in $^1/_4$ of the sphere (hkl, $\bar{h}kl$) under the same conditions as before for $3° \leq 2\theta \leq 60°$, yielding 2985 independent observed reflections. No violations of the I centering ($h + k + l = 2n + 1$ absent) were observed. A full-matrix least-squares refinement with anisotropic thermal parameters on the same eight atoms gave $R_1 = 11.79$ and $R_2 = 18.51$. This crystal was also studied at −190 °C by using a cryostat designed for the Syntex P$\bar{1}$. In this case, data were taken I centered, yielding 1270 peaks of $I \leq 2\sigma(I)$ for $3° \leq 2\theta \leq 45°$. The cell parameters changed to $a = 22.132$ (4) Å, $b = 13.276$ (3) Å, $c = 6.5725$ (9) Å, $\beta = 90.49$ (1)°, and $V = 1931.18$ Å^3. An anisotropic least-squares refinement gave $R_1 = 11.99$ and $R_2 = 20.42$ with Cl(6) weighted 0.67.

Discussion

The structure is derived from AABBCC... stacking of close-packed chloride ion layers with the c axis at an angle of 73° 24′ with the layers which is in excellent agreement with the calculated value of 72° 22′ based on a close-packed hard-sphere model. Zirconium ions are located between identical AA packed chloride ion layers to form an infinite planar sheet as illustrated in Figure 1. Each zirconium is located at the center of a trigonal prism of chloride ions, and the zirconiums are associated in triangles, each edge of which is doubly bridged by chloride ions. The triangles are joined by two chloride ion bridges at each vertex to form a ring of six Zr_3 units and an 11-Å diameter hole which, in the three-dimensional structure, results in an unbroken channel paralleling the c axis. This portion of the structure gives rise to a unit cell composition of $Zr_{12}Cl_{36}{}^{n+}$. The interatomic distances and angles for the monoclinic data are given in Table I, and positional and thermal parameters are give in Table II. Note that the zirconium triangles are not quite equilateral (Figure 2), the Zr(2)–Zr(2)′ distance being slightly longer than the two Zr(1)–Zr(2,2)′ distances.

Although the crystallographic data unambiguously yields the formula $[Zr_{12}Cl_{36}]^{n+}$ for the unit cell of the zirconium backbone, attempts to precisely locate the remaining aluminum and chlorine species which are contained in the channel were unsuccessful owing to their disorder. The two holes in the unit cell have a volume large enough to accommodate 28 close-packed chloride ions. However, the ideal stoichiometry requires 15.0 chlorides in the two holes, so this volume is only

Table II. Positional and Thermal Parameters for Eight Crystallographically Independent Atoms of $Zr_{12}Al_4Cl_{51}$

atom	x	y	z	atom	x	y	z
Zr(1)	0.0845 (1)	0.0000 (0)	0.4165 (5)	Cl(3)	0.1036 (3)	0.1246 (5)	0.1422 (10)
Zr(2)	0.2091 (1)	0.1279 (2)	0.2921 (3)	Cl(4)	0.2697 (4)	0.0000 (0)	0.4882 (14)
Cl(1)	0.0208 (4)	0.0000 (0)	0.7353 (13)	Cl(5)	0.2284 (5)	0.0000 (0)	0.0195 (14)
Cl(2)	0.1450 (3)	0.1249 (5)	0.6091 (9)	Cl(6)	0.2279 (7)	0.2515 (9)	0.0111 (16)

atom	U_{11}, Å^2	U_{22}, Å^2	U_{33}, Å^2	U_{12}, Å^2	U_{13}, Å^2	U_{23}, Å^2
Zr(1)	0.0175 (1)	0.0216 (2)	0.0178 (9)	0.0000 (0)	0.0000 (2)	0.0000 (0)
Zr(2)	0.0225 (1)	0.0225 (2)	0.0215 (7)	−0.0015 (1)	0.0000 (1)	0.0027 (2)
Cl(1)	0.0175 (2)	0.0809 (9)	0.0231 (24)	0.0000 (0)	0.0000 (5)	0.0000 (0)
Cl(2)	0.0300 (1)	0.0315 (4)	0.0251 (16)	−0.0045 (2)	0.0052 (4)	−0.0080 (6)
Cl(3)	0.0250 (1)	0.0459 (5)	0.0324 (17)	−0.0015 (2)	−0.0045 (4)	0.0201 (7)
Cl(4)	0.0250 (2)	0.0270 (6)	0.0391 (25)	0.0000 (0)	−0.0082 (5)	0.0000 (0)
Cl(5)	0.0475 (2)	0.0432 (7)	0.0249 (22)	0.0000 (0)	0.0134 (6)	0.0000 (0)
Cl(6)	0.2050 (6)	0.1052 (11)	0.0640 (31)	−0.1140 (7)	−0.0358 (11)	0.0317 (15)

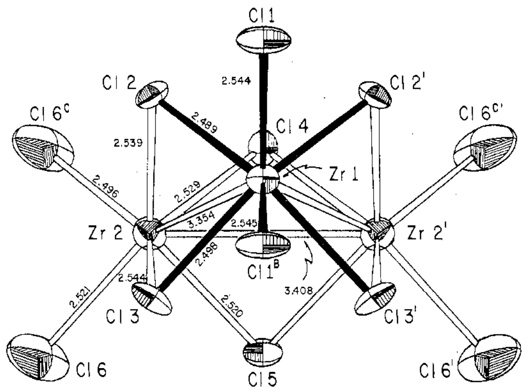


Figure 2. ORTEP drawing of the zirconium atom triangle showing both intra- and intertriangular chloro bridges and the trigonal-prismatic coordination of the metal atoms.

about half occupied. Ideally the two holes also contain 4.0 Al(III) atoms.

In an effort to locate the missing atoms, difference maps were run on all three monoclinic data sets by using refined positional and anisotropic thermal parameters for the eight known crytallographically independent atoms; all gave essentially the same results. The multiplicities of the zirconium and chlorine atoms of the backbone were also refined to determine if systematic absences or packing faults existed. We found the multiplicities of both the zirconium and chlorine atoms to be between 0.98 and 1.0, indicating no such absences or faults.

In addition, a third crystal, examined by rotation photographs after the completion of preceding studies, revealed *b*-axis doubling. Triclinic data were taken to determine whether the Al–Cl species were ordered in this case. The zirconium–chlorine backbone was not altered in structure or symmetry and refined anisotropically to an R_1 value of 15.92. The higher value suggests that the backbone is better modeled by the monoclinic cell. Difference maps of these data again resulted in a large number of peaks in the hole, and attempts were made to order the peaks into a physically meaningful model. The few peaks in the hole which stand out correspond to electron densities of 2.5 and 3.5 e/Å^2. The abnormally large thermal ellipsoids of the four Cl(6) suggest that these atoms are involved with the aluminum species which reside in the hole. Several attempts were made to test this hypothesis. When Cl(6) is weighted as two-thirds of an atom and the two peaks in the hole closest to Cl(6) are weighted as one-sixth of a chlorine each, the low-temperature isotropic thermal parameter for Cl(6) is reduced from 5.4 Å^2 to 2.3 Å^2, while those for two peaks in the hole are 2.6 and 2.9 Å^2. This implies that Cl(6) is disordered to one of the other two positions one-third of the time. However, this model, refined anisotropically, still gave a final R_1 of 11.99. However a tetrahedrally coordinated aluminum displaced from the center of the hole was found. This aluminum represents a partially disordered species and was weighted 0.25. This tetrahedral arrangement of peaks appears consistently in all triclinic difference maps and suggests that part of the aluminum is present as $AlCl_4^-$ or $Al_2Cl_7^-$ moieties. Attempts to refine a model of this type for the triclinic data set repeatedly gave very large thermal parameters for the hole peaks. Isotropic refinement of the structure including 0.5 aluminum and 7.25 chlorines/hole gave an R_1 of 14.44, and refinements of this structure which were anisotropic on the backbone and isotropic on the hole peaks gave an R_1 of 13.13. Further attempts to include more aluminum gave an R_1 of 13.08 but resulted in negative values for some of the anisotropic thermal parameters of the backbone. Nevertheless, the view that some of the hole species are bound to the backbone with Cl(6) intertriangular bridges forming part of the chlorine coordination sphere about the aluminum is supported by the results of these studies. It is possible that the $AlCl_4$ and/or Al_2Cl_7 in the hole are located with respect to the bridging Cl(6) such that the coordination environment about the aluminum approaches that in solid aluminum chloride (CN 6). Such an interaction could account for the large thermal ellipsoids for Cl(6) as well as the somewhat longer Zr(2)–Zr(2)′ distance. On the other hand the Cl′ atoms have more normal thermal ellipsoids and are reminiscent of a similar bridge in solid $ZrCl_4$[11]

The comparison of the infrared spectrum of the cluster with the spectra of zirconium trichloride,[12] various tetrachloroaluminates,[13–16] and aluminum chloride[16] should be useful in distinguishing between Zr–Cl and Al–Cl frequencies in the cluster. Although the zirconium atoms in the trichloride and cluster differ in formal oxidation state and in site group symmetry, the frequencies observed are all due to Cl–Zr–Cl bridging modes. The spectrum of zirconium trichloride shows frequencies at (in cm^{-1}) 350 sh, 340 ms, 270 w, 223.5 vs, 175 m, and 160 m while the cluster has frequencies (in cm^{-1}) at 469 s, 440 w, 417 w, 404 w, 370 m, br, 345 m, 320 w, 290 m, and 240 vs. Even taking into account that the frequencies would shift with a change in metal oxidation state, it seems clear that none of the frequencies above 400 cm^{-1} are related to the Zr–Cl modes. However, the strong absorption at 469 cm^{-1} in the cluster may be related to the $AlCl_4$ moiety which is variously reported to fall between 480 and 490 cm^{-1} in ionic compounds. In the cluster where we postulate that the Al–Cl moieties interact with the bridging chlorides, the reduced frequency should be expected. In the spectrum[16] of solid $AlCl_3$ there is a very strong absorption at 320 cm^{-1} which may be related to the weak band at the same position in the cluster.

The X-ray data indicate that the zirconium atoms lie in crystallographically differing sites in a ratio of 2:1, yet the composition of the cluster formally requires the presence of nine Zr(III) (d^1) and three Zr(IV) (d^0) atoms, giving a formal average charge of $Zr^{3.25+}$ on each zirconium. There is no way to rationally distribute identifiable zirconium oxidation-state ions in the unit cell, so the cluster must be viewed as a mixed-oxidation-state species with the nine d electrons delocalized over all the zirconium sites. The metal–metal distances are too long to invoke direct metal–metal interactions although they are shorter than the distances calculated for an equivalent hard-sphere model. That some other exchange pathway exists is shown by the magnetic properties of the cluster. The magnetic susceptibility exhibits an essentially temperature-independent paramagnetism of a very low magnitude for a compound containing nine d electrons per formula unit. The corrected molar susceptibility is about 1.55×10^{-4} cgsu at 3.86 kG over the temperature range of 300–80 K, while below 80 K it rises and reaches 2.00×10^{-4} cgsu at 5 K. These data are suggestive of the existence of cooperative phenomenon which decreases the susceptibility far below that expected for a compound containing magnetically isolated ions of Zr(III) which have a spin–orbit coupling constant of about 500 cm^{-1}.

Acknowledgment. This work was supported in part by the Research Committee of the Graduate School from funds supplied by the Wisconsin Alumni Research Foundation and in part by a National Science Foundation Departmental In-

---

(11) Krebs, B. *Z. Anorg. Allg. Chem.* **1970**, *378*, 263–272.

(12) Clemmer, R. G. Ph.D. Thesis, University of Wisconsin—Madison, Madison, WI, 1977.

(13) Brinkman, F. J.; Gerding, H. *Inorg. Nucl. Chem. Lett.* **1970**, *6*, 801–806.

(14) Brinkman, F. J.; Gerding, H. *Inorg. Nucl. Chem. Lett.* **1971**, *7*, 667–673.

(15) Carlson, G. L. *Spectrochim. Acta* **1963**, *19*, 1291–1307.

(16) Moyer, J. W. Ph.D. Thesis, University of Wisconsin—Madison, Madison, WI, 1971.

Inorg. Chem. **1980**, *19*, 3175–3176

strument Grant (Grant No. 28233) which allowed the purchase of the automated diffractometer. We are indebted to Mr. Clifford Feldman for the magnetic susceptibility data and to Dr. Laurence Hoard for additional consultation on the crystal structure.

Registry No. Aluminum zirconium chloride, 74231-09-7.

Supplementary Material Available: Listing of structure factor amplitudes (8 pages). Ordering information is given on any current masthead page.

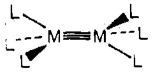
Contribution from the Department of Chemistry and the
Molecular Structure Center, Indiana University,
Bloomington, Indiana 47405

Tris(*N*,*N*′-dimethylethylenediamido)dimolybdenum (M≡M). A Metallopropellane with a Near-Eclipsed Central Mo_2N_6 Moiety

Timothy P. Blatchford, Malcolm H. Chisholm,*[1] Kirsten Folting, and John C. Huffman

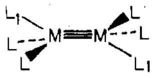
Received May 20, 1980

Albright and Hoffmann[2] recently made the provocative claim "triple-bonded ethane-like M_2L_6 transition metal complexes should be eclipsed". The compounds in question are of the general type **1** and **2**, in which the triple bond ($\sigma^2\pi^4$)



1

M = Mo, W
L = CH_2SiMe_3, NMe_2, OR



2

M = Mo, W
L = NMe_2, L_1 = halide or alkyl

is formed by the interaction of metal valence atomic orbitals of a and e symmetry.[3] The rationale for the preference for the eclipsed geometry rests on Albright and Hoffmann's calculation that overlap of the π-type atomic orbitals is favored in that configuration relative to the structurally observed staggered geometries. A test of this prediction by the synthesis of a $L_3M{\equiv}ML_3$ molecule with small monodentate ligands will probably not be forthcoming since, as the steric bulkiness of L decreases, polymeric ML_3 compounds are formed.[4] We wish here to report the synthesis of a new d^3–d^3 M≡M dimer which, by the use of three bridging *N*,*N*′-dimethylethylenediamido ligands, has a virtually eclipsed Mo_2N_6 skeleton. A structural comparison between a staggered and an eclipsed ethane-like M_2L_6 (M≡M) compound is now possible.

The reaction between 1,2-$Mo_2Cl_2(NMe_2)_4$ and 2 equiv of the monolithiated *N*,*N*′-dimethylethylenediamine leads, in the presence of excess free diamine, to the formation of $Mo_2(MeNCH_2CH_2NMe)_3$. The reaction is carried out in hexane at −78 °C, and the title compound is purified by vacuum sublimation (98 °C, 10^{-4} torr) followed by crystallization from hexane.[5] $Mo_2(MeNCH_2CH_2NMe)_3$ shows a strong molecular ion in the mass spectrometer and has a simple two-line ^1H NMR spectrum which is indicative of a bridged and time-averaged eclipsed structure. The *N*-methyl and *N*-CH_2 signals are shifted upfield and downfield, respectively, from positions they would otherwise have had in the absence of the magnetic anisotropy associated with the Mo-to-Mo triple bond.[6]

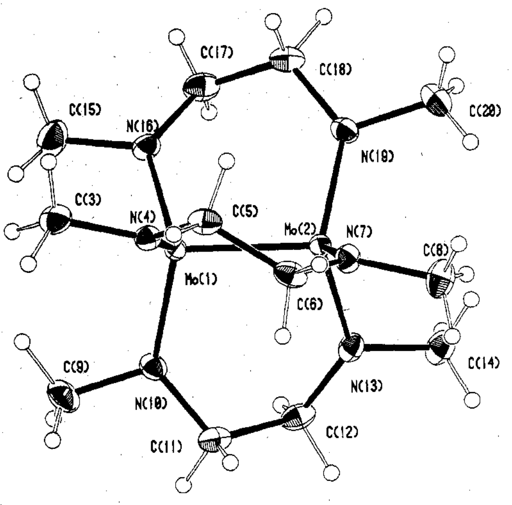


Figure 1. An ORTEP view of the $Mo_2(MeNCH_2CH_2NMe)_3$ molecule showing the atomic numbering scheme used in Tables I and II. Atoms are represented by thermal ellipsoids drawn at the 50% probability level.

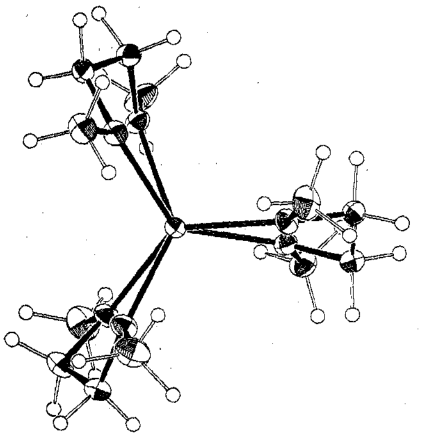


Figure 2. An ORTEP view of the $Mo_2(MeNCH_2CH_2NMe)_3$ molecule viewed down the Mo≡Mo bond emphasizing the near-eclipsed geometry of the Mo_2N_6 moiety. The deviation from the eclipsed conformation is given by the torsional angles listed in Table II.

Table I. Bond Distances (Angstroms)

A	B	dist	A	B	dist
Mo(1)	Mo(2)	2.190 (1)	N(10)	C(9)	1.467 (4)
Mo(1)	N(4)	1.969 (2)	N(10)	C(11)	1.452 (4)
Mo(1)	N(10)	1.964 (2)	N(13)	C(12)	1.456 (4)
Mo(1)	N(16)	1.961 (2)	N(13)	C(14)	1.458 (4)
Mo(2)	N(7)	1.967 (2)	N(16)	C(15)	1.458 (4)
Mo(2)	N(13)	1.967 (2)	N(16)	C(17)	1.459 (4)
Mo(2)	N(19)	1.971 (2)	N(19)	C(18)	1.456 (4)
N(4)	C(3)	1.463 (4)	N(19)	C(20)	1.444 (4)
N(4)	C(5)	1.447 (4)	C(5)	C(6)	1.518 (4)
N(7)	C(6)	1.458 (4)	C(11)	C(12)	1.512 (4)
N(7)	C(8)	1.456 (4)	C(17)	C(18)	1.512 (4)

---

(1) Camille and Henry Dreyfus Teacher-Scholar, 1979–1984.

(2) Albright, T. A.; Hoffmann, R. *J. Am. Chem. Soc.* **1978**, *100*, 7736. See also: Dedien, A; Albright, T. A.; Hoffmann, R. *Ibid.* **1979**, *101*, 3141. Calculations by others have implied little or no conformational preference for these molecules: Hall, M. B. *Ibid.* **1980**, *102*, 2104. Bursten, B. E.; Cotton, F. A.; Green, J. C.; Seddon, E. A.; Stanley, G. G. *Ibid.* **1980**, *102*, 4579.

(3) (a) For a recent review of the chemistry of these compounds, see: Chisholm, M. H.; Cotton, F. A. *Acc. Chem. Res.* **1978**, *11*, 356. (b) The detailed electronic structures have been reviewed: Cotton, F. A. *Ibid.* **1978**, *11*, 225.

(4) Successive replacement of Me_2N ligands by Cl ligands leads to polymeric $MoCl_3$: Akiyama, M.; Chisholm, M. H.; Cotton, F. A.; Extine, M. W.; Murillo, C. A. *Inorg. Chem.* **1977**, *16*, 2407.

(5) All operations were carried out by using dry and oxygen-free solvents and atmospheres.

(6) ^1H NMR data obtained in toluene-d_8 solution at 220 MHz: $\delta(CH_3)$ = 2.87, $\delta(CH_2)$ = 3.80; δ in ppm relative to $(CH_3)_4Si$. For a discussion of the diamagnetic anisotropy associated with the triple bond, see the discussion in ref 8.

0020-1669/80/1319-3175$01.00/0