Cl, F)[11] compounds that P–S distances are a function of the properties of the X groups depending perhaps on electronegativity and/or π-bonding ability. Since the order of electronegativities of C, N, and Cl varies wildly[12] with the method by which they are estimated, it is questionable whether the position of the present P–S distance (between 1.940 (2) Å for X = CH_3 and 1.885 (5) Å for X = Cl) is understandable on the basis of electronegativities alone or not. According to Pauling-type electronegativities (C, 2.55; N, 3.04; Cl, 3.16) there is at least a qualitative correlation.

The most interesting structural feature is the variation in P–N distances. It will be recalled that the 24 chemically equivalent P–N distances for $P_4(NMe)_6$ in the two crystallographically distinct molecules[3] have a mean value of 1.695 (12) Å. In the $SP_4(NMe)_6$ molecule (see Table VI) there are three chemically distinct sorts of P–N distance. For each type the mean values obtained in the two polymorphs agree quite well. It is found that type c (Table VI), which corresponds to the type present exclusively in $P_4(NMe)_6$, has the same length, namely, 1.70 (1) Å. Type b may be slightly longer, viz., 1.73 (2) Å, but the errors are such that this cannot be considered at all certain. Those of type a, however, with a mean value of 1.63 (2) Å, can be considered shorter with at least 95% confidence.

We believe that this kind of shortening is certainly to be expected on either, or both, of two grounds. First, the increase in the formal oxidation state of the phosphorus atom when a sulfur atom is attached should lead to a decrease in its covalent radius. Data for the two series PX_3, SPX_3, and OPX_3 (X = F, Cl)[13] suggest that such an effect might account for 0.03–0.04 Å of shortening. Second, polarity in the P–S bond in the sense P^+S^- would tend to increase the amount of π-electron density drawn from the nitrogen atoms to the phosphorus atom. This enhancement of the P–N π-bond order would also shorten the P–N bond. At present we shall not try to evaluate the relative importance of these two possible contributions since this could only be done by using other than structural methods, such as spectra of various sorts and calculations.

One encounters here the same lack of precision in atomic positions as in the cases of $P_4(NMe)_6O_4$ and $P_4(NMe)_6S_4$.[3] This seems to be a general problem, characteristic of this class of compounds, and we attribute it both to the globularity of the molecules—which in the extreme case leads to the existence of a plastic phase, as observed for $P_4(NMe)_6$—and also to the absence of a central atom linking the various P and N atoms together *across* the cage, which therefore can be envisioned as a rather soft, quasi-spherical structure, easily deformed under the action of the crystal packing forces. The crystal packing, shown in Figures 2 and 3, does not show any unusual contacts. Actual calculation of all intermolecular distances <4.0 Å showed none <3.2 Å. This is not inconsistent with attributing molecular distortions to intermolecular contacts since the distortions themselves relieve potentially bad intermolecular contacts.

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Registry No. $SP_4(NCH_3)_6$, 38448-57-6.

Supplementary Material Available: Listings of observed and calculated structure factors (11 pages). Ordering information is given on any current masthead page.

References and Notes

(1) (a) Texas A&M University. (b) Laboratoire de Chimie Minerale Moleculaire.

(2) F. A. Cotton, J. M. Troup, F. Casabianca, and J. G. Riess, *Inorg. Chim. Acta*, **11**, 33 (1974).

(3) Part 1: F. Casabianca, F. A. Cotton, J. G. Riess, C. E. Rice, and B. R. Stults, *Inorg. Chem.*, **17**, 3232 (1977).

(4) Part 3: F. A. Cotton, J. G. Riess, C. E. Rice, and B. R. Stults, *Inorg. Chem.*, to be submitted for publication.

(5) Part 4: F. A. Cotton, J. G. Riess, and B. R. Stults, to be submitted for publication.

(6) A. Wolff and J. G. Riess, *Bull. Soc. Chim. Fr.*, 1587 (1973); F. Casabianca, A. A. Pinkerton, and J. G. Riess, *Inorg. Chem.*, **16**, 864 (1977).

(7) F. A. Cotton, B. A. Frenz, G. Deganello, and A. Shaver, *J. Organomet. Chem.*, **50**, 227 (1973).

(8) Computer programs used on a PDP 11/45 computer at the Molecular Structure Corp., College Station, Texas, were those of the Enraf-Nonius structure determination package.

(9) D. T. Cromer and J. T. Waber, "International Tables for X-ray Crystallography", Vol. IV, Kynoch Press, Birmingham, England, 1974, Table 2.2B.

(10) D. T. Cromer, "International Tables for X-ray Crystallography", Vol. IV, Kynoch Press, Birmingham, England, 1974, Table 2.3.1.

(11) K. Karakida and K. Kuchitsu, *Inorg. Chim. Acta*, **16**, 29 (1976).

(12) A *different* position for nitrogen is obtained in *each* of the following cases: Allred-Rochow, N > Cl > C; Pauling, Cl > N > C; Mulliken, Cl > C > N. Cf. F. A. Cotton and G. Wilkinson, "Advanced Inorganic Chemistry", 3rd ed., Wiley, New York, 1972, p 115.

(13) T. Moritani, K. Kuchitsu, and Y. Morino, *Inorg. Chem.*, **10**, 344 (1971).

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A Binuclear Tantalum Compound Containing Bridging 1,2-Dimethyl-1,2-diimidoethene Formed by Dimerization of Acetonitrile

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Received June 12, 1978

It has been shown that a compound previously reported as $[TaCl_3(CH_3CN)_2]_2$ can be recrystallized from tetrahydrofuran (THF) to give $[TaCl_3(THF)_2]_2({=}NC(CH_3){=}C(CH_3)N{=})$. The crystal structure shows a centrosymmetric molecule with octahedrally coordinated tantalum atoms, $TaCl_3(THF)_2({=}N{—})$, bridged by an ethylene derivative formed by dimerization of CH_3CN. This compound can be treated with CH_3CN to regenerate the starting material, thus implying that the latter is actually $[TaCl_3(CH_3CN)_2]_2({=}NC(CH_3){=}C(CH_3)N{=})$, as suggested by McCarley. The structure found here is analogous to the one reported by McCarley for a niobium analogue. The characteristic crystallographic parameters are space group $P\bar{1}$, $a = 7.764$ (3) Å, $b = 13.910$ (3) Å, $c = 7.412$ (2) Å, $\alpha = 88.42$ (2)°, $\beta = 98.33$ (3)°, $\gamma = 103.27$ (3)°, $V = 770.9$ (4) Å^3, and $Z = 1$.

The work reported here represents the somewhat unexpected outcome of an attempt we made to characterize potential starting materials for the synthesis of some organotantalum compounds. In 1972 Kepert and co-workers reported a substance to which they assigned the formula $[TaCl_3(CH_3CN)_2]_2$ and for which they proposed a structure incorporating a double bond between the metal atoms. The possibility of this latter structural feature focused our interest on this particular compound and we considered it worthwhile to determine its crystal structure. No suitable crystals were

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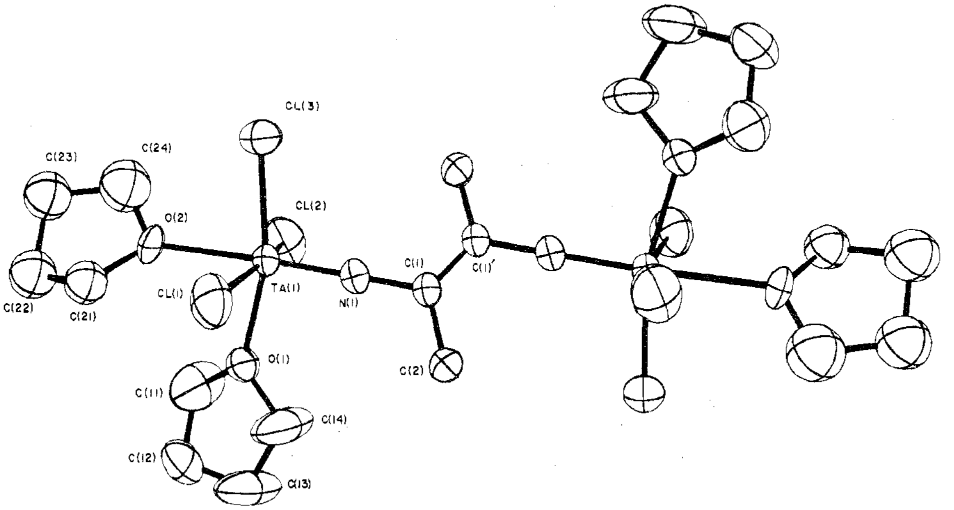


Figure 1. An ORTEP drawing of the molecule. Each atom is represented by its ellipsoid of thermal vibration scaled to enclose 50% of its electron density. The numbering scheme used in the tables is defined.

obtained until tetrahydrofuran (THF) was used as a solvent, but preliminary tests showed that these contained THF and therefore differed from the starting material. Nonetheless, we proceeded with a crystal structure determination, the results of which are presented here. Only after this structure was solved and partially refined did we recognize the relationship of this tantalum compound, whose formula was by then seen to be $Ta_2Cl_6[NC(CH_3)C(CH_3)N](THF)_4$, to the Nb and Ta compounds described by McCarley and co-workers[2] in 1975.

Experimental Section

Synthesis and Crystal Preparation. The green compound "$[TaCl_3(MeCN)_2]_2$", prepared by the method of Kepert et al.,[1] was dissolved in THF, giving a maroon solution. Approximately 100 mL of this solution was filtered into a separate flask, and an upper layer of 100 mL of hexane was gently placed over it using a syringe. After several days, as the hexane slowly diffused into the THF, well-formed, plate-shaped crystals appeared in the bottom of the flask. One of these crystals, of approximate dimensions 0.5 × 0.2 × 0.09 mm, was sealed in a capillary, in mineral oil, and used for data collection. All manipulations were performed under an inert atmosphere, and all solvents were dried and deoxygenated by standard methods.

The crystalline compound so obtained was shown (see below) by X-ray crystallography to be $[TaCl_3(THF)_2]({=}NC(CH_3){=}C(CH_3)N{=})$. When this compound is redissolved in acetonitrile and the solution slowly evaporated, the original "$[TaCl_3(CH_3CN)_2]_2$" precipitates. These two compounds have infrared spectra (recorded in mineral oil mulls on a Unicam SP 1100 spectrometer) with the following bands (cm^{-1}), considered to be localized in the bridging ligand, in common: 1108 (w), 725 (s, br), 660 (s, sp).

Data Collection. Preliminary photographic examination indicated that the crystals are triclinic, and ω scans on the diffractometer of several reflections showed the crystal to be of good quality. The following cell constants were obtained by centering on 15 intense reflections in the range $15° < 2\theta < 30°$: $a = 7.764$ (3) Å, $b = 13.910$ (3) Å, $c = 7.412$ (2) Å, $\alpha = 88.42$ (2)°, $\beta = 98.33$ (3)°, $\gamma = 103.27$ (3)°, $V = 770.9$ (4) Å^3. For $Z = 1$ and a formula weight of 951.15 the calculated density is 2.049.

Data were collected at 20 ± 2 °C on a Syntex $P\bar{1}$ diffractometer using Mo Kα radiation. The θ–2θ scan technique was employed using a variable scan rate of 4.0–24.0°/min with a scan range of 0.9° below Kα_1 to 0.9° above Kα_2. Reflections were collected in the range $0° < 2\theta < 48°$, and a total of 2068 with intensity $>3\sigma$ were obtained. The intensities of three standard reflections, measured every 100 reflections, showed no change with time. Lorentz and polarization corrections were applied to the data as was an empirical absorption correction based on ψ scans of seven reflections.

Structure Solution. The Ta position was easily determined from the three-dimensional Patterson function and refined by least-squares methods, assuming the space group to be $P\bar{1}$. Subsequent difference maps revealed the rest of the structure. It was found in this way that the molecular formula of the compound is $Ta_2Cl_6(CH_3CN{-}CNCH_3)(C_4H_8O)_2$. It was found that the carbon atoms of one THF molecule were twofold disordered. These four disordered atoms were refined as eight atoms each with an occupancy of $^1/_2$.

Table I. Positional Parameters for $[TaCl_3(THF)_2]_2({=}NC(CH_3){=}C(CH_3)N{=})$

atom	x	y	z
Ta(1)	0.15091 (4)	0.28733 (2)	0.40891 (5)
Cl(1)	0.0704 (4)	0.1773 (2)	0.6522 (5)
Cl(2)	0.3065 (4)	0.3710 (3)	0.1742 (4)
Cl(3)	−0.1174 (4)	0.2224 (2)	0.2163 (5)
O(1)	0.4135 (7)	0.3119 (5)	0.5648 (8)
O(2)	0.2445 (5)	0.1524 (5)	0.3020 (11)
N(1)	0.0943 (9)	0.3912 (5)	0.489 (1)
C(1)	0.047 (1)	0.4735 (6)	0.557 (1)
C(2)	0.111 (1)	0.4973 (7)	0.757 (1)
C(11)	0.571 (1)	0.2868 (12)	0.527 (2)
C(12)	0.678 (2)	0.2814 (10)	0.717 (2)
C(13)	0.359 (2)	0.6390 (14)	0.185 (2)
C(14)	0.462 (2)	0.3703 (14)	0.728 (2)
C(21)	0.273 (3)	0.063 (2)	0.444 (3)
C(22)	0.382 (4)	0.013 (2)	0.331 (4)
C(23)	0.333 (6)	0.011 (3)	0.216 (6)
C(24)	0.183 (4)	0.107 (2)	0.145 (4)
C(25)	0.182 (4)	0.061 (3)	0.305 (4)
C(26)	0.250 (4)	0.010 (2)	0.148 (4)
C(27)	0.349 (3)	0.061 (2)	0.094 (4)
C(28)	0.339 (4)	0.164 (2)	0.116 (4)

The structure was then refined by the full-matrix least-squares method, with all atoms treated anisotropically except those which were disordered. The final values of R_1 and R_2 were 0.036 and 0.052, respectively, and the error in an observation of unit weight was 1.231. Anomalous dispersion effects were included in the calculated structure factors for all atoms. A table of structure factors is available as supplementary material.

Computer programs used in the structure solution and refinement were those of the Enraf-Nonius structure determination package on a PDP 11/45 computer. All procedures, definitions, and sources of data required in the structure solution and refinement have been discussed and referenced elsewhere.[3]

Results

The positional parameters of all atoms are listed in Table I and the thermal parameters in Table II. Figure 1 shows the overall structure and defines the numbering scheme. Only one orientation of the disordered THF carbon atoms, C(21)–C(24), is shown. The second disordered orientation is obtained by replacing atoms C(21)–C(24) with atoms C(25)–C(28). The inversion center lies in the center of the C(1)–C(1)′ bond. The bond distances and angles are listed

Table II. Thermal Parameters for $[TaCl_3(THF)_2]_2(=NC(CH_3)=C(CH_3)N=)$

atom	B_{11}[a]	B_{22}	B_{33}	B_{12}	B_{13}	B_{23}
Ta(1)	4.32 (1)	3.46 (1)	3.61 (1)	2.21 (1)	−0.48 (1)	−0.96 (1)
Cl(1)	7.2 (1)	4.1 (1)	7.7 (2)	1.3 (1)	1.4 (1)	1.1 (1)
Cl(2)	9.9 (1)	9.3 (2)	4.2 (1)	5.1 (1)	2.2 (1)	0.8 (1)
Cl(3)	6.7 (1)	8.0 (1)	9.2 (2)	3.90 (9)	−3.8 (1)	−4.6 (1)
O(1)	3.5 (2)	4.8 (3)	4.3 (3)	2.0 (2)	0.0 (2)	−0.9 (2)
O(2)	7.0 (3)	4.4 (2)	7.6 (4)	3.4 (2)	−1.8 (3)	−3.6 (2)
N1	3.7 (2)	3.6 (3)	4.3 (3)	1.8 (2)	−0.1 (2)	−0.6 (3)
C(1)	3.3 (3)	3.3 (3)	3.4 (3)	1.5 (2)	0.3 (2)	−0.4 (3)
C(2)	5.6 (4)	5.1 (4)	3.5 (4)	2.9 (3)	−0.8 (3)	−1.4 (3)
C(11)	4.5 (4)	14.7 (8)	13.3 (9)	4.8 (4)	−0.5 (5)	−7.5 (6)
C(12)	5.8 (5)	7.0 (6)	9.3 (8)	3.2 (4)	−1.4 (5)	−0.1 (6)
C(13)	5.5 (5)	19 (1)	6.5 (6)	5.2 (6)	−2.1 (5)	−5.5 (7)
C(14)	9.0 (6)	21 (1)	13.5 (8)	9.2 (6)	−6.9 (6)	−121 (6)

atom	B_{iso}, Å^2	atom	B_{iso}, Å^2	atom	B_{iso}, Å^2
C(21)	5.4 (4)	C(24)	8.5 (7)	C(27)	6.3 (5)
C(22)	7.2 (6)	C(25)	8.6 (8)	C(28)	7.5 (6)
C(23)	8.8 (12)	C(26)	7.2 (7)		

[a] The form of the anisotropic thermal parameter is $\exp[-\frac{1}{4}(B_{11}h^2a^{*2} + B_{22}k^2b^{*2} + B_{33}l^2c^{*2} + 2B_{12}hka^*b^* + 2B_{13}hla^*c^* + 2B_{23}klb^*c^*)]$.

Table III. Selected Bond Distances (Å) for $[TaCl_3(THF)_2]_2(=NC(CH_3)=C(CH_3)N=)$[a]

Ta(1)–Cl(1)	2.392 (3)	C(13)–C(14)	1.48 (2)
–Cl(2)	2.386 (3)	C(14)–O(1)	1.43 (2)
–Cl(3)	2.353 (3)	O(2)–C(21)	1.64 (2)
Ta(1)–O(1)	2.151 (5)	O(2)–C(25)	1.26 (4)
–O(2)	2.356 (6)	O(21)–C(22)	1.56 (4)
Ta(1)–N(1)	1.747 (7)	C(25)–C(26)	1.59 (4)
N(1)–C(1)	1.405 (10)	C(22)–C(23)	1.57 (5)
C(1)–C(1)′	1.347 (16)	C(26)–C(27)	1.56 (5)
C(1)–C(2)	1.513 (11)	C(23)–C(24)	1.59 (5)
O(1)–C(11)	1.41 (1)	C(27)–C(28)	1.46 (4)
C(11)–C(12)	1.54 (2)	C(24)–O(2)	1.31 (3)
C(12)–C(13)	1.45 (2)	C(28)–O(2)	1.64 (3)

[a] Figures in parentheses are esd's occurring in the least significant digit.

Table IV. Selected Bond Angles (deg) for $[TaCl_3(THF)_2]_2(=NC(CH_3)=C(CH_3)N=)$[a]

Cl(1)–Ta(1)–Cl(2)	161.9 (1)	C(2)–C(1)–C(1)′	124.5 (10)
–Cl(3)	93.3 (1)	C(11)–O(1)–C(14)	106.6 (9)
–O(1)	83.4 (2)	O(1)–C(11)–C(12)	103.4 (11)
–O(2)	83.3 (2)	C(11)–C(12)–C(13)	102.8 (10)
–N(1)	98.2 (3)	C(12)–C(13)–C(14)	104.8 (11)
Cl(2)–Ta(1)–Cl(3)	95.7 (1)	C(13)–C(14)–O(1)	108.8 (12)
–O(1)	83.9 (2)	C(21)–O(2)–C(24)	104 (2)
–O(2)	82.0 (2)	C(25)–O(2)–C(28)	101 (2)
–N(1)	96.0 (3)	O(2)–C(21)–C(22)	98 (2)
Cl(3)–Ta(1)–O(1)	165.0 (2)	O(2)–C(25)–C(26)	109 (3)
–O(2)	84.1 (2)	C(21)–C(22)–C(23)	95 (2)
–N(1)	98.2 (2)	C(25)–C(26)–C(27)	104 (2)
O(1)–Ta(1)–O(2)	81.0 (2)	C(22)–C(23)–C(24)	106 (2)
O(2)–Ta(1)–N(1)	96.2 (3)	C(26)–C(27)–C(28)	99 (3)
O(1)–Ta(1)–N(1)	176.7 (3)	C(23)–C(24)–O(2)	108 (2)
Ta(1)–N(1)–C(1)	178.7 (9)	C(27)–C(28)–O(2)	99 (2)
N(1)–C(1)–C(1)′	119.7 (9)		
–C(2)	115.9 (7)		

[a] Figures in parentheses are esd's occurring in the least significant digit.

in Table III and IV, respectively. Because of the disorder problem, carbon atoms C(21)–C(24) and C(25)–C(28) appear to participate in some unusual bond lengths and bond angles.

The structure consists of a van der Waals packing of centrosymmetric molecules, each of which forms the entire content of one unit cell. The tantalum atoms are equivalent, and each one is octahedrally coordinated by three chloride ions, two oxygen atoms of tetrahydrofuran molecules, and a nitrogen atom belonging to the central bridging ligand. The chlorine atoms form a meridional set and the oxygen atoms are mutually cis.

There are some interesting metal–ligand bond length variations. The Ta–Cl bonds that are trans to each other are, within experimental uncertainty, equal to each other at 2.389 (3) Å, while the one trans to a THF oxygen atom is significantly shorter, at 2.353 (3) Å. The two oxygen atoms are at enormously different (ca. 0.20 Å) distances from the tantalum atom, in accord with the fact that one of them is trans to a multiple bond, viz., Ta≡N. This sort of trans effect of multiple bonds is very well recognized.[4]

The two tantalum atoms are joined by a very unusual bridging bidentate ligand, for which the only precedent is to be found in the similar niobium compound whose structure has been described by McCarley and co-workers.[2] In Figure 2, the central portions of the two molecules are compared, and it may be seen that they are essentially identical. The slight difference (0.03 Å) in the N–C distances is of borderline significance statistically.

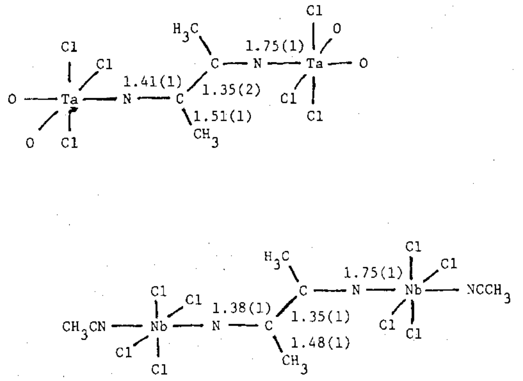
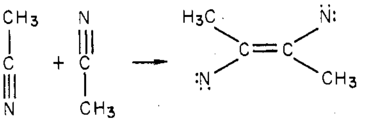


Figure 2. Schematic representations of the tantalum complex and its niobium analogue showing key bond lengths (Å) rounded to the nearest 0.01 Å.

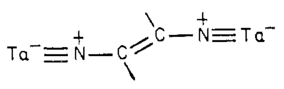
Discussion

The most remarkable feature of this compound is the bridging ligand connecting the two tantalum atoms. This obviously forms from two CH_3CN molecules, by a process formally represented in eq 1, with linkages to the tantalum atoms stabilizing the dimeric unit. On the basis of the formal structure shown for it in eq 1, these linkages to tantalum would

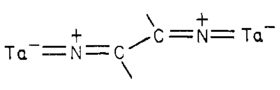


(1)

have to be multiple bonds in order to complete the octet at each nitrogen atom. Thus, the entire central chain could be described by the formal structure **1a**, where we also take into



1a



1b

account the fact that the Ta–N–C chain is essentially linear. The triple bond shown in **1a** is partly dative: two of the electron pairs result from electrons contributed by both the metal atom and the nitrogen atom while the third pair is donated by the nitrogen atom alone. The only other formal structure that is consistent with the geometry and provides an octet for each C and N atom is **1b** which leaves one unpaired electron formally on each tantalum atom. The central C–C distance observed is 1.35 (1) Å, and the standard C═C distance is 1.335 Å,[5] thus suggesting that **1a** alone may provide a good description of the bonding in this part of the molecule, with **1b** making at most a minor contribution. The C–CH_3 distance, 1.51 (1) Å, is exactly that expected for a single bond between sp^2 ($r \approx 0.74$ Å) and sp^3 ($r \approx 0.77$ Å) hybridized carbon atoms. The C–N distance, 1.41 (1) Å, is also consistent with expectation for a single bond between an sp hybridized nitrogen atom ($r < 0.70$ Å) and an sp^2 hybridized carbon atom ($r \approx 0.74$ Å).

Structure **1a** also implies that the multiplicity of the Ta–N bond is between double and triple, where the uncertainty arises because one component of the triple bond represented in **1a** is the result of electron donation by N to Ta and this need not be complete. The Ta–N distance, 1.75 (1) Å, while vastly shorter than Ta^V–N single-bond distances (~1.97 Å in $Ta(NMe_2)_2(O_2CNMe_2)_3$[6] for example), but not so short as some other M–N multiple-bond distances, where bond order should be 3.0 or nearly so, is not inconsistent with assigning a bond order >2.0.[7] In the case of $[(Me_3CCH_2)_3Ta{\equiv}CCMe_3]^-$ we have a Ta≡C triple bond to tantalum(V) and the distance is 1.76 (2) Å,[8] from which we might estimate that a full $Ta^V{\equiv}N$ bond should be ca. 1.70 Å. Thus, it is safe to say that **1a** can account satisfactorily for all the structural features of the tantalum compound, although a slight contribution from **1b** is possible.

One of the fascinating problems raised by this structure (and, of course, those of analogous niobium compounds) is how the metal atoms promote the dimerization of CH_3CN. The formal process is, after all, a highly unusual one and might have synthetic utility if properly controlled, modified, and exploited. McCarley has suggested that the active agent, either arising spontaneously by disproportionation of Ta^{IV} or introduced deliberately by reduction, is the trivalent metal atom. The trivalent species is then oxidized to the pentavalent state as the product is formed.

Another problem, perhaps more tractable, is to decompose the products in such a way as to recover the dimerized entity and regenerate a Nb^{III} or Ta^{III} species capable of reacting with more acetonitrile. Conceivably, a reductive cleavage reagent could be found so that the role of the metal could be made catalytic as shown, for example, in eq 2. Further studies to

$$2CH_3CN + 4[H] \xrightarrow{M^{III}} H_2NC(CH_3){=}C(CH_3)NH_2 \rightarrow \text{final products} \quad (2)$$

explore both the pre- and postchemistry of these interesting dinuclear complexes are being planned.

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Registry No. $[TaCl_3(THF)_2]_2({=}NC(CH_3){=}C(CH_3)N{=})$, 68024-53-3; $[TaCl_3(MeCN)_2]_2$, 34852-92-1.

Supplementary Material Available: A table of structure factors (9 pages). Ordering information is given on any current masthead page.

References and Notes

(1) D. G. Blight, R. L. Deutscher, and D. L. Kepert, *J. Chem. Soc., Dalton Trans.*, 87 (1972).
(2) P. A. Finn, M. Schaefer King, P. A. Kilty, and R. E. McCarley, *J. Am. Chem. Soc.*, **97**, 220 (1975).
(3) F. A. Cotton, B. A. Frenz, B. R. Stults, and T. R. Webb, *J. Am. Chem. Soc.*, **98**, 2768 (1976).
(4) E. M. Shustorovich, M. A. Porai-Koshits, and Y. A. Buslaev, *Coord. Chem. Rev.*, **17**, 1 (1975).
(5) *Chem. Soc., Spec. Publ.*, **No. 18** (1965).
(6) M. H. Chisholm, F. A. Cotton, and M. W. Extine, *Inorg. Chem.*, **17**, 2000 (1978).
(7) McCarley et al.[2] cite several pertinent comparisons.
(8) L. J. Guggenberger and R. R. Shrock, *J. Am. Chem. Soc.*, **97**, 2935 (1975).

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Crystal Structure of Tetrairidium Dodecacarbonyl, $Ir_4(CO)_{12}$. An Unpleasant Case of Disorder

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Tetrairidium dodecacarbonyl, $Ir_4(CO)_{12}$, has been investigated via a single-crystal X-ray diffraction study. The structure was solved using the trigonal space group $P3$, with $a = 13.290$ (3) Å, $c = 8.981$ (2) Å, $V = 1373.7$ (5) Å^3, and ρ(calcd) = 4.01 g cm^{-3} for mol wt 1105.0 and $Z = 3$. Data were collected with a Syntex $P2_1$ diffractometer and the structure was solved via Patterson, Fourier, and least-squares refinement techniques, yielding $R_F = 5.76\%$ and $R_{wF} = 4.65\%$ for 1172 reflections. The unit cell contains three distinct molecules of $Ir_4(CO)_{12}$, each of which lies on a threefold axis. There is a severe and complex disorder problem in that there is inversion disorder of $Ir_4(CO)_{12}$ molecules at two of these sites. There is a 0.833:0.167 disorder at site I (centered at 0, 0, ~0.176) and a 0.555:0.445 disorder at site III (centered at $^2/_3$, $^1/_3$, ~0.496), while site II (centered at $^1/_3$, $^2/_3$, ~−0.183) appears to be ordered. This disorder leads to problems in determining accurate atomic positions; however, the essential T_d symmetry of the $Ir_4(CO)_{12}$ molecule is confirmed and the average Ir–Ir bond length is found to be 2.693 Å.

Introduction

The trinuclear and tetranuclear "binary" carbonyls of the iron and cobalt subgroups have been subjected to intensive study via the method of single-crystal X-ray diffraction. *Accurate* crystal structures have now been reported for $Fe_3(CO)_{12}$,[1] $Ru_3(CO)_{12}$,[2] $Os_3(CO)_{12}$,[3] $Co_4(CO)_{12}$,[4] and $Rh_4(CO)_{12}$.[5] There has, however, been no report in the primary literature of the crystal structure of $Ir_4(CO)_{12}$. This

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