Despite the strong Ir–Br interaction in **2** there are no dramatic changes in the bond distances and angles of the PCBr ligand. A comparison of the dimensions of PCBr in **2** with those observed[9] in $Rh_2(O_2CCH_3)_3[(C_6H_4)P(C_6H_5)(C_6F_4Br)]\cdot PCB$ (**3**) suggests that there may be a slight lengthening of the C–Br bond (1.85 (2) and 1.92 (2) Å in **3** and **2**, respectively), but this is barely significant in a statistical sense.

The interaction between the iridium and bromine atoms is best described as a dative bond. This model results in what may be described as either a t_{2g}^6 or a rare-gas configuration at the Ir center assuming oxidation state +III. The assignment of the trivalent oxidation state (d^6 configuration) not only agrees with the observed diamagnetism but also entails a favorable comparison of the dimensions with those of an authentic Ir(III) halophosphine complex. For example, in *mer*-$IrCl_3P_3$[10] the Ir–Cl and Ir–P distances were reported to be 2.364 [3] and 2.373 [9] Å, respectively.

In light of the similarity of the ^{31}P NMR spectra, especially the inequality of the P sites and the large coupling constants, we propose that **1** is also an octahedral complex with a η^2-PCBr and a η^1-PCBr in trans configuration.

We believe that the existence of these new compounds confirms the expectation expressed by Crabtree et al.[3] that "the coordination chemistry of halocarbons will prove to be extensive, especially when part of a chelating ligand". It is worth noting that while the Crabtree compound had a P–C_6H_4Br chelating ligand, we have a P–C_6F_4Br ligand, where the donor ability of the bromine atom might be expected to be less. On the other hand, Crabtree was dealing with Ir^I while we have Ir^{III}, which would favor stronger $-Br\rightarrow Ir$ bonding in our case. Either these two factors are each of little importance or they offset each other fairly neatly, since the Ir–Br distances are virtually identical.

Acknowledgment. We thank the National Science Foundation and CAICYT for support.

Registry No. **1**, 103564-37-0; **2**, 103564-38-1.

Supplementary Material Available: Complete tables of bond distances and angles and anisotropic displacement parameters (3 pages); a listing of structure factors (12 pages). Ordering information is given on any current masthead page.

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Contribution from the Department of Chemistry
and Laboratory for Molecular Structure and Bonding,
Texas A&M University, College Station, Texas 77843

Preparation and Properties of the Tribromide of *trans*-Dibromotetrakis(acetonitrile)vanadium(III), $[VBr_2(CH_3CN)_4]Br_3$. A Symmetric Br_3^- Ion

F. Albert Cotton,* Gregg E. Lewis, and Willi Schwotzer

Received February 26, 1986

Recently in this laboratory we have been endeavoring to establish some compounds containing vanadium(II) in forms suitable for further synthetic chemistry in nonaqueous media. Some of this work has entailed the reinvestigation of promising looking compounds previously mentioned in the literature. In some cases the reported compounds have been confirmed and further characterized, while in others the compounds have required reformulation.[1] We have been interested not only in establishing accurately the composition and structures of these compounds but also in confirming or finding convenient preparative procedures for them.

Table I

formula	$Br_5VN_4C_8H_{12}$
fw	614.70
space group	$C2/m$
syst absences	hkl, $h + k = 2n + 1$
a, Å	14.851 (2)
b, Å	10.401 (2)
c, Å	6.309 (1)
β, deg	104.35 (1)
V, Å^3	944.1 (3)
Z	2
d_{calcd}, g/cm^3	2.162
cryst size, mm	0.3 × 0.4 × 0.5
μ(Mo Kα), cm^{-1}	109.84
data colln instrum	Syntex P$\bar{1}$
radiation (monochromated in incident beam)	Mo Kα (λ = 0.71073 Å)
orientation reflcns, no., range	15, $30 < 2\theta < 50$
temp, °C	5
scan method	θ–2θ
data colln range deg	$4 < 2\theta < 50$
no. of unique data, total with $F_o^2 > 3\sigma(F_o^2)$	838, 669
no. of params refined	48
transmissn factors (exptl): max, min	0.998, 0.380
R^a	0.031
R_w^b	0.042
quality-of-fit indicator^c	0.994
largest shift/esd, final cycle	0.02
largest peak, e/Å^3	0.507

[a] $R = \sum||F_o| - |F_c||/\sum|F_o|$. [b] $R_w = [\sum w(|F_o| - |F_c|)^2/\sum w|F_o|^2]^{1/2}$; $w = 1/\sigma^2(|F_o|)$. [c] Quality of fit $= [\sum w(|F_o| - |F_c|)^2/(N_{observns} - N_{params})]^{1/2}$.

Table II. Positional Parameters and Their Estimated Standard Deviations for $[VBr_2(CH_3CN)_4]Br_3$[a]

atom	x	y	z
Br(1)	0.13205 (5)	0.000	0.3183 (1)
Br(2)	0.500	0.000	1.000
Br(3)	0.17379 (6)	0.500	1.1786 (1)
V	0.000	0.000	0.000
N	−0.0653 (3)	−0.1407 (4)	0.1450 (6)
C(1)	−0.1030 (3)	−0.2110 (5)	0.2278 (8)
C(2)	−0.1521 (5)	−0.3002 (6)	0.336 (1)

[a] Estimated standard deviations in the least significant digits are shown in parentheses.

The compound $VBr_2\cdot CH_3CN$ and the reported electrochemical preparation[2] of it were of interest in this regard, and we have examined this chemistry. As will be discussed in detail later, our work has led to the isolation of a crystalline compound that has been shown by X-ray crystallography to be $[VBr_2(CH_3CN)_4]Br_3$.

Experimental Section

All chemical operations were conducted in an atmosphere of argon. Acetonitrile was dried over P_2O_5, distilled immediately before use, and transferred via syringe. The vanadium rod was obtained from Alfa Products and measured 6.2 mm × 7.5 cm. The platinum wire was also obtained from Alfa Products and measured 0.25 mm × 15.5 cm. A power pack capable of delivering 5.0 V dc at 3.0 A was used.

Synthesis and Crystallization of $[VBr_2(CH_3CN)_4]Br_3$. The solution phase consisted of 60 mL of acetonitrile, 10 mg of tetrabutylammonium perchlorate, and 1 mL of bromine. The vanadium anode and platinum cathode were 1 cm apart, and the voltage was applied for 8–72 h, resulting in large orange-brown crystals on the surface of the anode as well as in the bottom of the reaction vessel. The composition and structure of this compound have been determined by X-ray crystallography, showing it to be $[VBr_2(CH_3CN)_4]Br_3$.

Structure Solution and Refinement. The positions of the vanadium and bromine atoms were located by using direct methods in the form of the MULTAN program. All other atoms were located in difference Fourier maps. In all, 48 variable parameters were fitted to 669 observations. The final least-squares cycles did not shift any parameter by more than 0.02

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(2) Habeeb, J.; Neilson, L.; Tuck, D. G. *Can. J. Chem.* **1977**, *55*, 2631.

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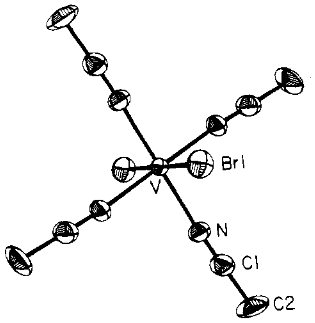

Figure 1. ORTEP view of $[VBr_2(CH_3CN)_4]^+$, at the 50% probability level.

Table III. Bond Distances (Å) and Angles (deg) in $[VBr_2(CH_3CN)_4]Br_3$

	Distances		
Br(1)-V	2.435 (1)	C(1)-C(2)	1.452 (9)
V-N	2.087 (4)	Br(2)-Br(3)	2.548 (1)
N-C(1)	1.126 (7)		
	Angles		
Br(1)-V-N	90.30 (9)	V-N-C(1)	176.0 (4)
N-V-N′	89.0 (2)	N-C(1)-C(2)	179.2 (6)

times its estimated standard deviation. The refinement gave residuals (defined and summarized in Table I) of $R = 0.031$ and $R_w = 0.042$ and goodness-of-fit = 0.994. A final difference Fourier map following refinement exhibited random peaks as high as 0.51 e/Å^3. The positional parameters are listed in Table II.

Results and Discussion

The structure of the compound, *trans*-$[VBr_2(CH_3CN)_4]Br_3$, is presented in Figure 1, and the important dimensions are listed in Table III. Both the cation and the Br_3^- ion have crystallographic C_{2h} $(2/m)$ symmetry. The cation has very nearly D_{4h} symmetry, except for very slight deviations of the N-V-N, V-N-C, and N-C-C angles from 90, 180, and 180°, respectively.

The Br_3^- Ion. Although this ion is much less stable or common than its congener I_3^- and does not, for example, exist in aqueous solution, it has been structurally characterized in several crystalline compounds (Table IV). In the present compound we have the only reported case of a completely symmetrical Br_3^- ion, i.e., one that both is rigorously linear and has identical Br-Br distances. There was one reported earlier that resides on a crystallographic twofold axis and thus has equal bond lengths but deviates slightly from linearity. All of the others show significantly disparate bond lengths, although they deviate but little from linearity. It is notable that the greater the disparity in the bond lengths, the greater their sum.

The compound we have prepared and studied is not new. It was reported in 1965 by Hathaway and Holah,[3] who correctly deduced its constitution from a combination of its elemental analysis, visible spectrum, IR spectrum, and magnetic moment. Our X-ray work fully confirms their proposal. It is to be noted that, in Hathaway and Holah's work, vanadium metal reacted directed with a solution of bromine in acetonitrile, without the application of a potential. We have also found this to be true. The same product, $[VBr_2(CH_3CN)_4]Br_3$, was obtained by us whether a voltage was applied or not.

Table IV. Structure of the Tribromide Ion As Found Crystallographically in Six Compounds

compd	Br′-Br-Br″, deg	Br-Br′, Å	Br-Br″, Å	Br′···Br″, Å	ref
$[VBr_2(CH_3CN)_4]Br_3$	180[a]	2.548 (1)	2.548 (1)	5.096 (2)	*b*
$[(C_6H_5)_4P]Br_3$	177.62 (2)	2.5505 (4)	2.5505 (4)	5.1010 (6)	*c*
$[S_4N_3]Br_3$	179 (1)	2.677 (2)	2.431 (2)	5.108 (3)	*d*
$CsBr_3$	177.5 (5)	2.698 (6)	2.440 (6)	5.138 (9)	*e*
$[CS_3N_2Br]Br_3$	178.8 (1)	2.721 (1)	2.417 (2)	5.138 (2)	*f*
$[PBr_4]Br_3$	177 (1)	2.91 (1)	2.39 (1)	5.30 (2)	*g*

[a] Figure without esd implies an exact value required by symmetry. [b] This work. [c] Bogaard, M. P.; Rae, A. D. *Cryst. Struct. Commun.* **1982**, *11*, 175. [d] Mayerle, J. J.; Wolmershauser, G.; Street, G. B. *Inorg. Chem.* **1979**, *18*, 1161. [e] Breneman, G. L.; Willett, R. D. *Acta Crystallogr., Sect. B: Struct. Crystallogr. Cryst. Chem.* **1969**, *B25*, 1073. [f] Wolmershauser, G.; Krüger, C.; Tsay, Y.-H. *Chem. Ber.* **1982**, *115*, 1126. [g] Breneman, G. L.; Willett, R. D. *Acta Crystallogr.* **1967**, *23*, 467.

In view of our experience, we were puzzled by the earlier claim[2] that $VBr_2{\cdot}CH_3CN$ could be obtained under similar conditions. We therefore corresponded with Professor D. G. Tuck, who carried out an electrochemical reaction to produce a sample of what was presumed to be $VBr_2{\cdot}CH_3CN$. We examined this material crystallographically and found that it was $[VBr_2(CH_3CN)_4]Br_3$. It is to be noted that analysis for the element bromine, though simple to do, is essentially useless for distinguishing between the two formulas since the bromine percentages are 63.9% for $VBr_2{\cdot}CH_3CN$ and 65.0% for $[VBr_2(CH_3CN)_4]Br_3$. Professor D. G. Tuck has reinvestigated the preparative procedure and has found that in his laboratory the product now obtained is also $VBr_5{\cdot}4CH_3CN$; he has requested us to make it clear that there is now no disagreement between our two laboratories.

Acknowledgment. We thank the Robert A. Welch Foundation for support under Grant No. A-494 and Professor D. G. Tuck for his helpful comments and for supplying a sample.

Registry No. $[VBr_2(CH_3CN)_4]Br_3$, 103664-47-7; $VBr_2{\cdot}CH_3CN$, 64345-05-7.

Supplementary Material Available: A table of anisotropic displacement parameters (1 page); a listing of structure factors (4 pages). Ordering information is given on any current masthead page.

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(3) Hathaway, B. J.; Holah, D. G. *J. Chem. Soc.* **1965**, 537.

Contribution from the Department of Chemistry
and Laboratory for Molecular Structure and Bonding,
Texas A&M University, College Station, Texas 77843,
and Department of Chemistry, The Technion-Israel
Institute of Technology, Haifa, Israel

Derivatization of the Cuboidal Mo_4S_4–Aquo Ion: Preparation and Structure of $Mo_4S_4(HB(pz)_3)_4(pz)$ (pz = Pyrazolyl, $C_3N_2H_3^-$)

F. Albert Cotton,*[†] Zvi Dori,*[†‡] Rosa Llusar,[†]
and Willi Schwotzer[†]

Received February 12, 1986

The deliberate assembly of metal cluster compounds, starting from the composition of the core and extending to the choice of the ligand sphere, represents a synthetic challenge. Our own approach to the preparation of tri- and tetranuclear clusters of molybdenum and tungsten has in the past involved aqueous routes, because the aqueous chemistry of these elements is dominated by the presence of polynuclear species, many of them with M-M bonds.[1] These aquo species are attractive synthons since they are in essence composed of the cluster core surrounded by kinetically fairly labile water ligands.

Recently the cuboidal cluster aquo ion $[Mo_4S_4]_{aquo}$ has been prepared by Sykes[2] as well as by us[3] by different synthetic routes. In this paper we report the preparation of a derivative, $Mo_4S_4(HB(pz)_3]_4(\mu\text{-pz})$ (pz = pyrazolyl, $C_3N_2H_3^-$). The molecular compound is soluble in organic solvents, which demonstrates that the concept of cluster synthesis by aquo species does not restrict

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[†] Texas A&M University.
[‡] The Technion-Israel Institute of Technology.