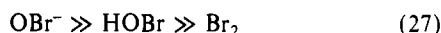


are 143, 244, and 251 kJ mol⁻¹ (25.0 °C), respectively. Although these bond energies are for a homolytic cleavage, they provide an approximation of the relative bond strengths for these species. We propose that Cl₂O reacts more rapidly with Ni^{II}(CN)₄²⁻ than either Cl₂ or HOCl because of the ease with which it can release Cl⁺.

An interesting comparison for the trend in eq 24 can be made with the trend in rates for the oxidation of Co^{II}L²⁻ complexes, where L = EDTA⁴⁻ or CyDTA⁴⁻ (*trans*-1,2-diaminocyclohexane-*N,N,N',N'*-tetraacetate), by OBr⁻, HOBr, and Br₂.^{43,44}



These reactions are postulated to proceed by an inner-sphere

electron-transfer mechanism that takes place with formation of radical intermediates, i.e. one-electron steps. Thus, there is no relation between the homolytic bond energies for the various bromine species and the trend observed in eq 27. Such a trend would be expected for an atom-transfer mechanism. For oxidation of Ni^{II}(CN)₄²⁻ by various chlorine species, the rate constants agree with such a trend, which implies the reaction proceeds by an oxidative-addition or atom-transfer mechanism.

Conclusions

Oxidation of Ni^{II}(CN)₄²⁻ by aqueous chlorine to form *trans*-Ni^{IV}(CN)₄(H₂O)₂⁻ proceeds via Cl₂O, Cl₂, and HOCl pathways. Cl₂O oxidizes Ni^{II}(CN)₄²⁻ 40 times faster than Cl₂ and 2.5 × 10⁷ times faster than HOCl. The ratio *k*_{Cl₂}/*k*_{HOCl} for this system is similar to that for oxidation of Pt^{II}(CN)₄²⁻, which gives a platinum(IV) product.⁹ This and thermodynamic considerations for the first step in the oxidation process suggest the three pathways proceed through formation of a highly reactive nickel(IV) intermediate.

Of the three pathways, the Cl₂O reaction is unique. Cl₂O has been shown to be an active chlorinating agent with a variety of organic reagents.^{19,45} However, to our knowledge this is the first time Cl₂O has been shown to be active in the oxidation of a metal-ligand complex in aqueous solution. It is an extremely effective oxidizing agent.

Acetic acid catalysis of Cl₂O formation from HOCl is confirmed, and the catalytic effect is even greater than previously observed.²³ The apparent rapid formation of Cl₂O from Cl₂ and HOCl in the presence of acetic acid merits additional study.

Acknowledgment. This work was supported by National Science Foundation Grant CHE-8720318.

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Metal-Metal Bonds Involving Vanadium Atoms. A Facile Synthesis of a Novel Divanadium Tetrakis(dithioacetate) That Contains Two μ-η²-S₂ Bridges from Bis(benzene)vanadium(0) and Dithioacetic Acid

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The reaction between bis(benzene)vanadium(0), (η⁶-C₆H₆)₂V, and dithioacetic acid, CH₃CSSH, furnishes a novel dimer, (CH₃CS₂)₂V(μ-η²-S₂)₂V(S₂CCH₃)₂, in 56-62% yields. The brown product has been characterized by elemental analyses, NMR, IR, and mass spectrometry, magnetic susceptibility measurements, and X-ray crystallography. The immediate coordination sphere of the two vanadium cores is best regarded as consisting of two distorted trigonal prisms that share the four sulfur atoms that form one rectangular face and have each of the other four rectangular faces capped by one sulfur atom. Because the new compound is diamagnetic and the V-V distance equals 2.800 (2) Å, a single metal-metal bond is postulated for this vanadium-vanadium d¹-d¹ pair. Therefore, each vanadium center has an unusual and rare nine-coordinate geometry, having the form of a tricapped trigonal prism. The compound crystallizes in space group *P2₁/c* with *a* = 10.425 (2) Å, *b* = 11.123 (2) Å, *c* = 9.133 (4) Å, β = 97.12 (2)°, *V* = 1051 (1) Å³, *Z* = 2, *R* = 0.0476, and *R_w* = 0.0598. Other important structural features: the S-S distance of the μ-η²-S₂ bridge is 1.997 (3) Å, and the V-S distances range from 2.366 (3) to 2.502 (2) Å.

Introduction

With the recognition that metal atoms form direct bonds, the preparation, structural characterization, and reactivity of transition-metal compounds containing M-to-M bonds have become areas of intense study.¹ In contrast to numerous, well-known dinuclear tetracarboxylates possessing quadruple M-to-M bonds such as M₂(μ-O₂CR)₄L₂ (M = Cr, Mo, W; R = alkyl or aryl

groups; L = σ-donor ligands, e.g., H₂O, THF, etc.),² as well as dithio analogues of the type Mo₂(μ-S₂CR)₄L₂ (R = CH₃, C₆H₅; L = THF),³ similar compounds (that would contain M-to-M bonds

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Table I. Crystallographic Data for $V_2(S_2)_2(S_2CCH_3)_4$

formula $V_2C_8H_{12}S_{12}$	$T = 20\text{ }^\circ\text{C}$
space group $P2_1/c$ (No. 14)	$\lambda = 0.71073\text{ \AA}$
$a = 10.425(2)\text{ \AA}$	$\rho_{\text{calcd}} = 1.880\text{ g cm}^{-3}$
$b = 11.123(2)\text{ \AA}$	$\mu = 20.008\text{ cm}^{-1}$
$c = 9.133(4)\text{ \AA}$	transm coeff = 0.9870–0.8015
$\beta = 97.12(2)^\circ$	$R = 0.0476$
$V = 1051(1)\text{ \AA}^3$	$R_w = 0.0598$
$Z = 2$	

of different multiplicity) of transition metals of the vanadium and titanium groups are not known.

As part of our interest in this field of early-transition-metal chemistry, we have begun to investigate reactions of low-valent, well-established organometallic sandwich type compounds, such as bis(benzene)vanadium(0) with various carboxylato-like ligands. We report here the reaction of $(\eta^6\text{-C}_6\text{H}_6)_2\text{V}$ toward dithioacetic acid, which gives the first example of a simple divanadium tetrakis(dithioacetate) containing two symmetrical $\mu\text{-}\eta^2\text{-S}_2$ bridges, i.e. $[(\text{CH}_3\text{CS}_2)_2\text{V}(\mu\text{-}\eta^2\text{-S}_2)_2\text{V}(\text{S}_2\text{CCH}_3)_2]$. The new compound possesses a single V–V bond with the distance of 2.800 (1) Å. This is an important finding since V-to-V bonds, single as well as multiple, are very rare.^{1,2} An unusual feature of the dimer is the chelating coordination of dithioacetates at each end of the V–V core; all other M–M-bonded dimeric carboxylates, including $\text{Mo}_2(\mu\text{-S}_2\text{CR})_4\text{L}_2$ compounds, contain bridging acidic groups. Additionally, the reaction constitutes the first exploitation of the reactivity of bis(benzene)vanadium(0).⁴ Finally, we compare our new product to a structurally similar compound $[(\text{Bu}_2\text{NCS}_2)_2\text{V}(\mu\text{-}\eta^2\text{-S}_2)_2\text{V}(\text{S}_2\text{CNBu}_2)_2]$, which was prepared by the reaction of VS_4^{3-} with tetraisobutylthiuram disulfide by Halbert, Hutchings, Rhodes, and Stiefel.⁵

Experimental Section

All operations of moisture- and air-sensitive materials were carried out under an inert atmosphere by employing standard Schlenk techniques and a double-manifold vacuum line. Solids were manipulated in a Vacuum Atmospheres Co. glovebox. Solvents were freshly distilled from benzophenone ketyl prior to use. Solutions were transferred via stainless steel cannulae and/or syringes. Bis(benzene)vanadium⁴ and dithioacetic acid⁶ were prepared according to literature methods. Elemental analyses were performed by Galbraith Microanalytical Laboratories. The NMR spectrum was recorded on a Varian FT-80A spectrometer. The IR spectrum was measured on a Perkin-Elmer 599B spectrophotometer. The mass spectrum was measured (direct insertion probe, 70 eV) on a Finnigan TSQ 45 mass spectrometer. The magnetic susceptibility was determined at room temperature on an MSB1 Johnson Matthey magnetic susceptibility balance. Corrections for diamagnetism were made with Pascal's constants.

Preparation of $V_2(S_2)_2(S_2CCH_3)_4$. A stirred solution of freshly sublimed bis(benzene)vanadium(0) (0.70 g, 3.4 mmol) in toluene (40 mL) in a 100-mL Schlenk tube is treated with redistilled dithioacetic acid (0.9 mL, 12.2 mmol) via syringe. The solution immediately changes color from red to dark brown. The reaction mixture is stirred at room temperature for 4 days. During this period, a dark brown crystalline solid is precipitated. The content of the Schlenk tube is concentrated to one-fourth of the original volume. Heptane (40 mL) is added, and the solution is cooled in a dry ice/acetone bath for 1.5 h to further the precipitation of the dark brown product. The product is filtered out, collected, and recrystallized from toluene/heptane (v/v 25/75) mixture. Reproducible yields of $V_2(\mu\text{-}\eta^2\text{-S}_2)_2(S_2CCH_3)_4$ are obtained: 0.56–0.62 g (56–62%). Anal. Calcd for $C_8H_{12}S_{12}V_2$: C, 16.16; H, 2.04. Found:

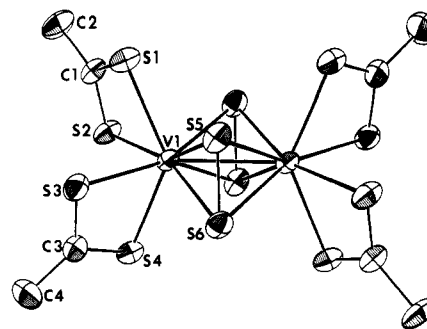


Figure 1. ORTEP drawing of the $V_2(\mu\text{-}\eta^2\text{-S}_2)_2(S_2CCH_3)_4$ molecule, which also defines the labeling scheme. The thermal ellipsoids enclose 50% of electron density.

Table II. Positional Parameters and Their Estimated Standard Deviations for $V_2(S_2)_2(\text{CH}_3\text{CSS})_4$ ^a

atom	x	y	z	B, Å ²
V(1)	0.6162 (1)	0.4723 (1)	0.0874 (1)	2.13 (3)
S(1)	0.5862 (2)	0.4420 (2)	0.3524 (2)	3.01 (5)
S(2)	0.7831 (2)	0.5814 (2)	0.2556 (2)	3.17 (5)
S(3)	0.7482 (2)	0.2901 (2)	0.1480 (2)	3.17 (5)
S(4)	0.8061 (2)	0.4647 (2)	-0.0551 (2)	3.24 (5)
S(5)	0.5733 (2)	0.6539 (2)	-0.0546 (2)	2.93 (5)
S(6)	0.4793 (2)	0.6368 (2)	0.1219 (2)	2.93 (4)
C(1)	0.7152 (9)	0.5306 (8)	0.3973 (9)	3.0 (2)
C(2)	0.761 (1)	0.556 (1)	0.5594 (9)	4.1 (2)
C(3)	0.8474 (8)	0.3341 (9)	0.0281 (9)	3.2 (2)
C(4)	0.965 (1)	0.265 (1)	-0.000 (1)	4.8 (3)

^a Anisotropically refined atoms are given in the form of the equivalent isotropic displacement parameter defined as $(4/3)[a^2\beta_{11} + b^2\beta_{22} + c^2\beta_{33} + ab(\cos \gamma)\beta_{12} + ac(\cos \beta)\beta_{13} + bc(\cos \alpha)\beta_{23}]$.

Table III. Bond Distances (Å) for $V_2(S_2)_2(\text{CH}_3\text{CSS})_4$ ^a

V(1)–V(1')	2.800 (2)	V(1)–S(5')	2.412 (3)	S(3)–C(3)	1.670 (9)
V(1)–S(1)	2.502 (2)	V(1)–S(6)	2.366 (3)	S(4)–C(3)	1.67 (1)
V(1)–S(2)	2.489 (3)	V(1)–S(6')	2.376 (2)	S(5)–S(6)	1.997 (3)
V(1)–S(3)	2.473 (3)	S(1)–C(1)	1.677 (9)	C(1)–C(2)	1.53 (1)
V(1)–S(4)	2.501 (3)	S(2)–C(1)	1.650 (9)	C(3)–C(4)	1.49 (1)
V(1)–S(5)	2.412 (3)				

^a Numbers in parentheses are estimated standard deviations in the least significant digits.

C, 16.48; H, 1.95. ¹H NMR (C_6D_6): δ 2.68 (s, 3 H). IR (KBr disk, cm^{-1}): 1804 (s), 1780 (s), 1665 (w), 1652 (m), 1638 (m), 1476 (m, br), 1426 (m), 1396 (m), 1373 (w), 1368 (w), 1359 (w), 1313 (s), 1294 (sh), 1291 (s), 1274 (w), 1011 (s), 1006 (s), 846 (m), 833 (s), 813 (w), 711 (m), 576 (s), 444 (s), 371 (m). MS (direct inserting probe, 70 eV): m/e 592 (100%, M – 2H), 296 (43%, M/2 – 1H), 230 (18%, V_2S_4), 91 (16%, CH_3CS_2). $\chi_M = -2.18 \times 10^{-4}$ cgsu.

Single crystals, suitable for X-ray diffraction studies, are grown by slow interdiffusion of heptane placed on top of a benzene solution of $V_2(S_2)_2(S_2CCH_3)_4$.

X-ray Crystallography. Single-crystal X-ray diffraction analyses were performed by application of general procedures that were previously described.⁷ The pertinent crystallographic data are summarized in Table I. X-ray diffraction data were collected at 20 °C on a $0.40 \times 0.20 \times 0.15$ mm crystal for 1450 unique reflections possessing $4 < 2\theta < 50^\circ$ and $h, k, \pm l$, on a RIGAKU AFC5R diffractometer utilizing graphite-monochromated Mo K α radiation, $\lambda = 0.71073$, and 2θ scans. By use of the Enraf-Nonius Structure Determination Package PLUS, the data were corrected for Lorentz, polarization, and absorption effects. The structure was solved by direct methods using a portion of the program SHELX-86 followed by difference Fourier syntheses. All eleven non-hydrogen atoms were refined anisotropically. Refinements were carried out by least-square methods using 100 variables and the 1046 data for which $I > 3\sigma(I)$. The quality-of-fit indicator was 1.223. The final difference Fourier map contained some residual electron density below $1\text{ e}/\text{\AA}^3$ in the immediate vicinity of the vanadium atoms; the largest peak was $0.80\text{ e}/\text{\AA}^3$.

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Table IV. Bond Angles (deg) for $V_2(S_2)_2(CH_3CSS)_4^a$

V(1)-V(1)-S(1)	112.21 (8)	S(2)-V(1)-S(3)	86.26 (9)	S(5)-V(1)-S(5)'	109.03 (9)
V(1)-V(1)-S(2)	137.18 (8)	S(2)-V(1)-S(4)	78.45 (8)	S(5)-V(1)-S(6)'	49.39 (8)
V(1)-V(1)-S(3)	136.56 (8)	S(2)-V(1)-S(5)'	89.56 (9)	S(5)-V(1)-S(6)	87.92 (8)
V(1)-V(1)-S(4)	113.30 (7)	S(2)-V(1)-S(5)	149.26 (9)	S(5)-V(1)-S(6)'	88.17 (9)
V(1)-V(1)-S(5)	54.50 (6)	S(2)-V(1)-S(6)	85.85 (9)	S(5)-V(1)-S(6)	49.29 (8)
V(1)-V(1)-S(5)'	54.53 (6)	S(2)-V(1)-S(6)'	159.5 (1)	S(6)-V(1)-S(6)'	107.61 (9)
V(1)-V(1)-S(6)	53.97 (6)	S(3)-V(1)-S(4)	68.57 (9)	V(1)-S(1)-C(1)	87.9 (3)
V(1)-V(1)-S(6)'	53.64 (7)	S(3)-V(1)-S(5)'	150.2 (1)	V(1)-S(2)-C(1)	89.0 (3)
S(1)-V(1)-S(2)	68.31 (8)	S(3)-V(1)-S(5)	88.59 (9)	V(1)-S(3)-C(3)	89.2 (3)
S(1)-V(1)-S(3)	78.81 (8)	S(3)-V(1)-S(6)	158.76 (9)	V(1)-S(4)-C(3)	88.2 (3)
S(1)-V(1)-S(4)	134.49 (9)	S(3)-V(1)-S(6)'	85.85 (8)	V(1)-S(5)-V(1)	70.97 (8)
S(1)-V(1)-S(5)	126.6 (1)	S(4)-V(1)-S(5)'	81.64 (9)	V(1)-S(5)-S(6)	64.10 (9)
S(1)-V(1)-S(5)	80.96 (8)	S(4)-V(1)-S(5)	127.21 (9)	V(1)-S(5)-S(6)'	64.43 (9)
S(1)-V(1)-S(6)	79.95 (8)	S(4)-V(1)-S(6)	128.7 (1)	V(1)-S(6)-V(1)	72.39 (8)
S(1)-V(1)-S(6)'	128.3 (1)	S(4)-V(1)-S(6)'	81.03 (9)	V(1)-S(6)-S(5)	66.5 (1)
V(1)-S(6)-S(5)	66.28 (9)	S(2)-C(1)-C(2)	125.6 (7)	S(3)-C(3)-C(4)	123.4 (7)
S(1)-C(1)-S(2)	114.8 (5)	S(3)-C(3)-S(4)	114.0 (5)	S(4)-C(3)-C(4)	122.5 (7)
S(1)-C(1)-C(2)	119.6 (7)				

^aNumbers in parentheses are estimated standard deviations in the least significant digits.

Results and Discussion

The reaction of bis(benzene)vanadium(0), $(\eta^6-C_6H_6)_2V$, and dithioacetic acid, CH_3CSSH , in toluene solution yields the new compound $V_2(S_2)_2(S_2CCH_3)_4$ in yields of up to 60%. This compound has been characterized by elemental analyses, IR, 1H NMR, and mass spectrometry, magnetic susceptibility measurements, and X-ray crystallography. The X-ray study shows that the new compound is composed of an ordered array of discrete dimeric molecules which reside on centers of inversion. A view of the entire molecular unit is depicted in Figure 1, which also defines the atom-labeling scheme. The final atomic positional and isotropic equivalent displacement parameters are presented in Table II, and interatomic distances and angles are listed in Tables III and IV, respectively.

The immediate coordination sphere of the two vanadium cores, viz., $S_4V(S_2)_2VS_4$, in $V_2(\mu-\eta^2-S_2)_2(S_2CCH_3)_4$, is best regarded as consisting of two distorted trigonal prisms that share the four sulfur atoms that form one rectangular face and have each of the other four rectangular faces capped by one sulfur atom. The V-to-V distance is 2.800 (2) Å and provides structural evidence for a direct metal-metal bond. Because the oxidation state of each vanadium atom is +4, we deal in this case with a d^1-d^1 system leading to a vanadium-vanadium single bond. Therefore, each vanadium center has an unusual and rare nine-coordinate geometry, having the form of a tricapped trigonal prism.

Only a few examples of metal-metal bonds between vanadium atoms are known.^{1,2} Thus, a shorter distance is found in the $(Pr^iC_5H_4)V(\mu-S)_2(\mu-\eta^1-S_2)V(Pr^iC_5H_4)$ ⁸ compound, in which the V-V bond order is also 1 (distance: 2.610 (1) Å), but this compound contains a different set of ligands with a higher concentration of negative charges between the two vanadium atoms. However, V=V bond distances of 2.400 (2) and 2.462 (2) Å in $V_2(PCH_3Ph)_4(H_2ZnH_2BH_2)_2$ ⁹ and $(C_5H_5)_2V_2(CO)_5$,¹⁰ respectively, as well as the V≡V bond distance of 2.200 (2) Å in V_2 - $(2,6$ -dimethoxyphenyl)₄,¹¹ are even shorter, as expected for higher bond orders. Further support for a V-V single bond in $V_2(\mu-\eta^2-S_2)_2(S_2CCH_3)_2$ comes from the following two observations: (1) the measurements of the bulk magnetic susceptibility show that the new compound is diamagnetic, and (2) the 1H NMR spectrum

of the new dimer has a very normal appearance, manifesting additional evidence that the two d^1 electrons are spin-paired.

With the new dimer described in this paper, there are now four structurally characterized compounds that are related. The other three, obtained from inorganic starting materials, are (1) the mineral patronite,^{12,13} $(VS_4)_m$ containing a repeating linear pattern, $[V(\mu-\eta^2-S_2)_2V'(\mu-\eta^2-S_2)_2V'']_m$, in which the V-V' distance is 2.83 Å, the V-V'' separation is 3.22 Å, the average S-S distance equals 2.03 Å, and the average V-S bond length is 2.40 Å, (2) the $V_2(\mu-\eta^2-S_2)_2(S_2CNBu^i)_4$ compound⁵ (yield 22%), in which the V-V distance is 2.851 (1) Å, the S-S distance of the S_2^{2-} ligand is 1.998 (2) Å, and the average V-S bond length equals 2.405 Å, and (3) the $V(S_2CCH_3)_4$ complex^{14,15} (yield 8%), which has two kinds of average V-S distances (owing to two independent molecules in the unit cell), $V-S_A$ and $V-S_B$ of 2.50 and 2.46 Å, respectively.

The important dimensions of our dimer, $V_2(\mu-\eta^2-S_2)_2(S_2CCH_3)_4$, are as follows: the V-V bond length equals 2.800 (1) Å, the S-S distance of the $\mu-\eta^2-S_2$ bridge is 1.997 (3) Å, and the V-S distances range from 2.366 (3) to 2.502 (2) Å. The S(2)-S(3) distance of 3.392 (2) Å is also important. Partial oxidation of the dithiolate could lead to sulfur-sulfur interaction in this position.

In conclusion, we demonstrate a new, facile synthetic method whereby a classical organometallic compound, bis(benzene)vanadium(0), can be utilized as an entry into the still underdeveloped chemistry of vanadium.

Acknowledgment. This research was supported by the donors of the Petroleum Research Fund, administered by the American Chemical Society. We also thank Cleveland State University for the Research Creative Activity Award and the Research Challenge grant approved by the Ohio Board of Regents for support of this work. We wish to thank Professor F. A. Cotton for helpful discussions and use of his X-ray diffractometer. Helpful discussions of this work with Professor J. P. Fackler, Jr., are also greatly appreciated. We acknowledge a gift of VCl_4 from Umetco Minerals Corp.

Supplementary Material Available: Table of anisotropic displacement parameters for $[V_2(S_2)_2(S_2CCH_3)_4]$ (1 page); a listing of observed and calculated structure factors (6 pages). Ordering information is given on any current masthead page.

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