Inorganica Chimica Acta, 165 (1989) 245–248

Spectroscopic and Electrical Properties of Oxidized Tris(dmit)vanadium Anion Complexes (dmit = 4,5-dimercapto-1,3-dithiole-2-thionate)

KAZUKI AKIBA and GEN-ETSU MATSUBAYASHI*

Department of Applied Chemistry, Faculty of Engineering, Osaka University, Yamadaoka, Suita, Osaka 565 (Japan)

and TOSHIO TANAKA

Department of Applied Physical Chemistry, Fukui Institute of Technology, Gakuen, Fukui 910 (Japan)

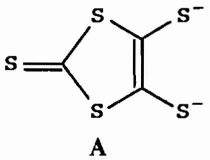
(Received May 25, 1989; revised July 21, 1989)

Abstract

Several oxidized tris(dmit)vanadium anion complexes ($dmit^{2-}$ = the 4,5-dimercapto-1,3-dithiole-2-thionate anion) were prepared; $[FeCp_2][V(dmit)_3]$ (Cp^- = the cyclopentadienyl anion), $[Fe(MeCp)_2][V(dmit)_3]$ ($MeCp^-$ = the methylcyclopentadienyl anion), $[Fe(Me_5Cp)_2][V(dmit)_3]$ (Me_5Cp^- = the pentamethylcyclopentadienyl anion), $[NiCp_2][V(dmit)_3]$, $Fe(V(dmit)_3]_2\cdot 3H_2O$, and $Co(V(dmit)_3]\cdot 3H_2O$. They behave as semiconductors with electrical conductivities of 1×10^{-7} to 1×10^{-4} S cm^{-1} measured for compacted pellets at 25 °C. On the basis of powder electronic reflectance, IR, ESR, and X-ray photoelectron spectra, electronic states of the complexes and interactions among the anion moieties are discussed.

Introduction

Planar metal complexes with the 4,5-dimercapto-1,3-dithiole-2-thionate ligand (dmit; A), $[M(dmit)_2]^{n-}$ complexes (M = Ni, Pd, and Pt; $n < 1$), have attracted much attention owing to their high electrical conductivities [1–5]; $[TTF][Ni(dmit)_2]_2$ (TTF = tetrathiafulvalene) [3], $[NMe_4][Ni(dmit)_2]_2$ [4] and $[TTF][Pd(dmit)_2]_2$ [5] were reported to become superconductors at low temperatures. Two- or three-dimensional molecular interactions through sulfur atoms are considered to be most important for metallic and superconducting properties of these dmit–metal complexes and of charge transfer compounds of sulfur-rich organic donors [1, 6]. From the view that cubic tris(dmit)metallate anion complexes are also expected to behave as new conductors upon oxidation through multi-dimensional dmit–dmit interactions in the solid state, we have recently reported preparations and properties of some tris(dmit)vanadium anion complexes [7].



A

This paper reports preparations of oxidized $V(dmit)_3$ complexes with several cations as well as their electrical properties and discusses their electronic states on the basis of powder electronic reflectance, IR, ESR, and X-ray photoelectron spectra.

Experimental

Materials

$FeCp_2$ (Cp^- = the cyclopentadienyl anion), $NiCp_2$, $Fe(MeCp)_2$ ($MeCp^-$ = the methylcyclopentadienyl anion), $Fe(Me_5Cp)_2$ (Me_5Cp^- = the pentamethylcyclopentadienyl anion), $Fe(ClO_4)_3\cdot 9H_2O$, $Co(ClO_4)_2\cdot 6H_2O$ and $Cu(ClO_4)_2\cdot 6H_2O$ were commercially available. 4,5-Bis(benzoylthio)-1,3-dithiole-2-thione [8], $[NBu^n_4]_2[Zn(dmit)_2]$ [5], $[NBu^n_4]_2[V(dmit)_3]$ [7] and $[NiCp_2][PF_6]$ [9] were prepared according to the literature methods.

$[FeCp_2][PF_6]$ was prepared by reaction of $FeCp_2$ with a concentrated aqueous nitric acid solution, followed by addition of an aqueous solution of $[NH_4][PF_6]$. $[Fe(MeCp)_2][PF_6]$ and $[Fe(Me_5Cp)_2][PF_6]$ were also prepared by a similar procedure.

Preparation of $[M][V(dmit)_3]$ ($[M]^+ = [FeCp_2]^+$ (1), $[Fe(MeCp)_2]^+$ (2), $[Fe(Me_5Cp)_2]^+$ (3) and $[NiCp_2]^+$ (4))

All the procedures for preparation of the following complexes were performed under nitrogen atmosphere.

---

*Author to whom correspondence should be addressed.

0020-1693/89/$3.50

© Elsevier Sequoia/Printed in Switzerland

An acetonitrile (4 cm^3) solution of $[FeCp_2][PF_6]$ (13 mg, 40 μmol) was added to an acetonitrile (10 cm^3) solution of $[NBu^n_4]_2[V(dmit)_3]$ (14 mg, 12 μmol) with stirring to give a green precipitate of **1**. The product was collected by centrifugation, washed with acetonitrile and dried *in vacuo* (50% yield). *Anal.* Calc. for $C_{19}H_{10}FeS_{15}V$: C, 27.63; H, 1.22. Found: C, 28.07; H, 1.59%. By a similar procedure, reactions of $[NBu^n_4]_2[V(dmit)_3]$ with $[Fe(MeCp)_2][PF_6]$, $[Fe(Me_5Cp)_2][PF_6]$ or $[NiCp_2][PF_6]$ afforded dark green microcrystals of **2** (24% yield), **3** (30% yield) and **4** (31% yield), respectively. *Anal.* **2**, Calc. for $C_{21}H_{14}FeS_{15}V$: C, 29.53; H, 1.66. Found: C, 29.76; H, 1.81%. **3**, Calc. for $C_{29}H_{30}FeS_{15}V$: C, 36.04; H, 3.14. Found: C, 35.49; H, 3.09%. **4**, Calc. for $C_{19}H_{10}NiS_{15}V$: C, 27.53; H, 1.22. Found: C, 27.31; H, 1.49%.

Preparation of Fe[V(dmit)$_3$]$_2$·3H$_2$O (5) and Co[V(dmit)$_3$]·3H$_2$O (6)

An acetonitrile (4 cm^3) solution of $Fe(ClO_4)_3 \cdot 9H_2O$ (21 mg, 41 μmol) was added to an acetonitrile (10 cm^3) solution of $[NBu^n_4]_2[V(dmit)_3]$ (17 mg, 15 μmol) with stirring to afford dark green microcrystals of **5**. The product was collected by centrifugation, washed with acetonitrile and dried *in vacuo* (47% yield). *Anal.* Calc. for $C_{18}H_6FeO_3S_{30}V_2$: C, 15.56; H, 0.44. Found: C, 15.30; H, 0.49%.

By a similar procedure, complex **6** was obtained by the reaction of $[NBu^n_4]_2[V(dmit)_3]$ with $Co(ClO_4)_2 \cdot 6H_2O$ (13% yield). *Anal.* Calc. for $C_9H_6CoO_3S_{15}V$: C, 14.36; H, 0.80. Found: C, 14.09; H, 0.78%.

The presence of metals in these complexes was confirmed by X-ray fluorescence analysis. The presence of water in complexes **5** and **6** was confirmed by ^1H NMR spectra.

Physical Measurements

Electrical conductivities were measured for compacted pellets in the −30 to +25 °C range by the conventional two-probe method [10]. Electronic absorption, powder electronic reflectance [10], IR, ESR [11], and X-ray photoelectron spectra (XPS) [11, 12] were recorded as described elsewhere.

Results and Discussion

Spectroscopic Properties of Oxidized Tris(dmit)vanadium Anion Complexes

$[NBu^n_4]_2[V(dmit)_3]$ is stably oxidized by one-electron at a low potential ($E_{1/2}^0 = 0.15$ V versus SCE) in electrolysis, as is illustrated in its cyclic voltammogram in acetonitrile and the absorption spectral changes under electrolysis [7]. Figure 1 shows the absorption spectra of $[NBu^n_4]_2[V(dmit)_3]$ on addition of $[FeCp_2][PF_6]$ with various concentrations in acetonitrile. The spectral change is essentially the same as that in the potential-controlled electrolysis; the intense band at 500 nm decays on addition of the $[FeCp_2]^+$ ion, a band concomitantly occurring at 390 nm [7]. This finding indicates the formation of the one-electron oxidized species, $[V(dmit)_3]^-$, in solution, through oxidation by the ferrocenium cation ($FeCp_2/[FeCp_2]^+$, $E_{1/2}^0 = 0.328$ V versus SCE) [13]. Addition of Fe^{3+} or Co^{2+} ion to an acetonitrile solution of $[NBu^n_4]_2[V(dmit)_3]$ has caused the same spectral change as the above system. Reactions of $[NBu^n_4]_2[V(dmit)_3]$ with several oxidizing compounds have given the stable oxidized $V(dmit)_3$ complexes **1**–**6**.

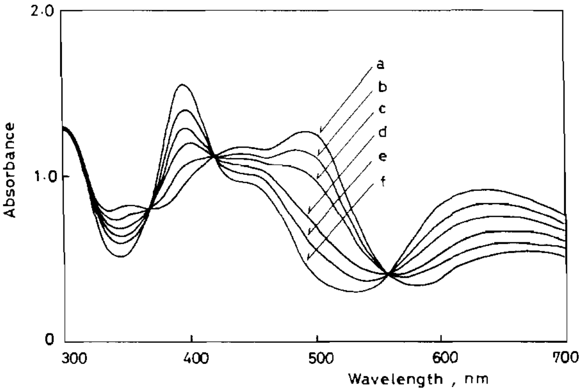


Fig. 1. Electronic absorption spectra of $[NBu^n_4]_2[V(dmit)_3]$ (6.67×10^{-5} mol dm^{-3}) in acetonitrile in the presence of $[FeCp_2][PF_6]$: (a) 0, (b) 0.77×10^{-5}, (c) 2.30×10^{-5}, (d) 3.78×10^{-5}, (e) 4.59×10^{-5}, (f) 7.56×10^{-5} mol dm^{-3}.

The valence state of the vanadium atom of the complexes can be deduced from binding energies of vanadium 2p electrons determined by XPS, which are summarized in Table 1. Binding energies of 2p electrons of **1**–**4** are very close to that of $[NBu^n_4]_2[V(dmit)_3]$, indicating that these complexes are essentially in the vanadium(IV) valence state, dmit-centered oxidation occurring. However, complexes **5** and **6** exhibit somewhat large binding energies com-

TABLE 1. Binding energies of V 2p electrons determined from XPS and ν(C=C) stretching frequencies of the dmit ligand of the complexes

Complex	Binding energy of V $2p_{3/2}$ electrons (eV)	ν(C=C) (cm^{-1})
$[NBu^n_4]_2[V(dmit)_3]$	523.3	1440
1	523.4	1340
2	523.7	1330
3	523.4	1350
4	523.4	1250
5	523.9	1280
6	524.1	1250

TABLE 2. Binding energies (eV) of metal 2p electrons determined from XPS

Complex	Fe $2p_{3/2}$	Ni $2p_{3/2}$	Co $2p_{3/2}$
1	710.2		
$[FeCp_2][PF_6]$	711.5		
$FeCp_2$	709.3		
2	711.0		
$[Fe(MeCp)_2][PF_6]$	711.5		
$Fe(MeCp)_2$	709.4		
3	709.4		
$[Fe(Me_5Cp)_2][PF_6]$	709.3		
$Fe(Me_5Cp)_2$	707.8		
4		855.6	
$[NiCp_2][PF_6]$		856.9	
$NiCp_2$		855.5	
5	711.9		
$FeSO_4$	711.5		
$Fe_2(SO_4)_3$	714.0		
6			780.3
$CoCl_2\cdot 6H_2O$			782.4
Co metal			779.0

pared with the other complexes, suggesting some oxidation of the vanadium atom through metal-to-ligand electron transfer. Table 2 lists binding energies of metal 2p electrons of complexes **1**–**6** together with those of metal ions, metallocenes and metallocenium salts. On the basis of these binding energies, complexes **5** and **6** are suggested to contain Fe(II) and Co(I) ions together with the $[V(dmit)_3]^-$ anion, respectively. In complex **2** the binding energy of Fe 2p electrons is close to that of the $[Fe(MeCp)_2]^+$ cation and the corresponding binding energy of **3** is essentially the same as that of the $[Fe(Me_5Cp)_2]^+$ cation. On the other hand, the binding energy of 2p electrons of complex **1** falls between those of $FeCp_2$ and the $[FeCp_2]^+$ cation, suggesting some charge transfer from the $[V(dmit)_3]^-$ moiety to the $[FeCp_2]^+$ cation through an anion–cation interaction in the solid state. In complex **4** the binding energy of Ni 2p electrons is greatly lowered compared with that of the $[NiCp_2]^+$ cation. This finding suggests a negative charge transfer from the $[V(dmit)_3]^-$ moiety to the $[NiCp_2]^+$ cation. In accordance with this, further oxidation of the dmit ligand of the $[V(dmit)_3]^-$ moiety is observed, as described below.

The oxidation state of the dmit ligand of dmit–metal complexes can be deduced from the C=C stretching frequency in IR spectra, as reported previously [14]. $[NBu^n_4]_2[V(dmit)_3]$ exhibits a ν(C=C) stretching band at 1440 cm^{-1}, whereas **1**–**3** give a strong band at 1330–1350 cm^{-1} (see Table 1). Lowering of the ν(C=C) stretching frequencies by *c.* 100 cm^{-1} corresponds to one-electron oxidation of the $[V(dmit)_3]^{2-}$ anion. On the other hand, complexes **4**–**6** exhibit bands near 1250 cm^{-1}, suggesting that these complexes contain further oxidized dmit moieties.

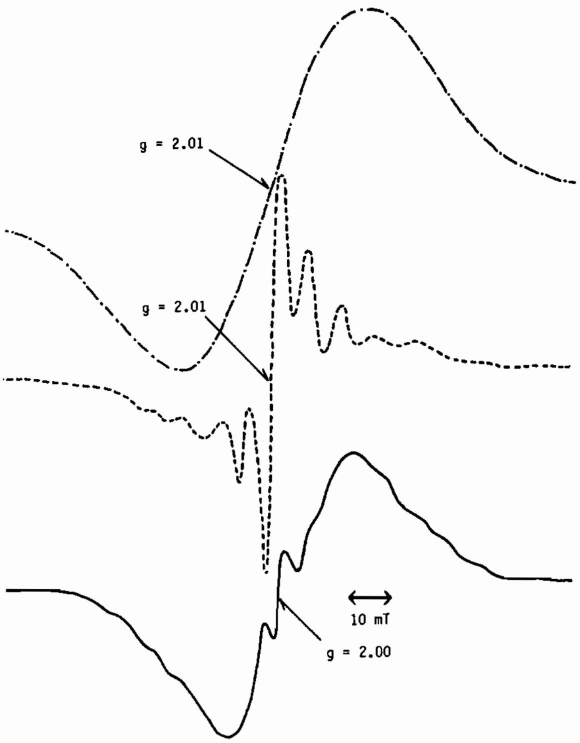


Fig. 2. Powder ESR spectra of $[NBu^n_4]_2[V(dmit)_3]$ (——), $[NiCp_2][V(dmit)_3]$ (**4**) (–·–), and $Fe[V(dmit)_3]_2$ $3H_2O$ (**5**) (- - -) measured at room temperature.

$[NBu^n_4]_2[V(dmit)_3]$ shows a broad powder ESR signal due to the typical vanadium(IV) species, as illustrated in Fig. 2. The oxidized complexes **1**–**3** exhibit no obvious ESR signals. Although the vanadium atoms of these complexes are considered to be essentially in a vanadium(IV) state on the basis of binding energies of vanadium 2p electrons, the unpaired electrons on the oxidized dmit ligand are coupled with an electron on the vanadium atom to afford no appreciable signal. Moreover, no detectable ESR signals of $[FeCp_2]^+$, $[Fe(MeCp)_2]^+$ and $[Fe(Me_5Cp)_2]^+$ cations have been measured, as it was reported to be difficult to detect signals of these cations [15]. In complexes **4**–**6** in which the dmit moieties are further oxidized, intense ESR signals are observed. They are ascribed to the signals due to the vanadium(IV) species (see Fig. 2).

Figure 3 shows the powder reflectance spectra of complexes **1** and **4**, together with that of $[NBu^n_4]_2[V(dmit)_3]$. The spectrum of $[NBu^n_4]_2[V(dmit)_3]$ displays bands which correspond to those measured in solution [7]. However, **1** exhibits a broad band near 800 nm. This seems to indicate a molecular interaction among $[V(dmit)_3]^-$ anion moieties. In the spectrum of complex **4**, a broad band appears at

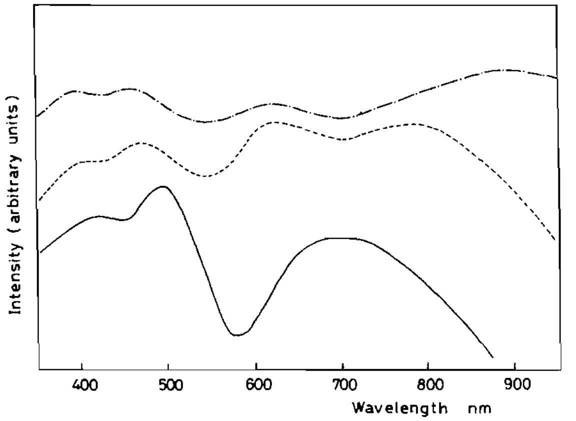


Fig. 3. Powder electronic reflectance spectra of $[NBu^n_4]_2$-$[V(dmit)_3]$ (——), $[FeCp_2][V(dmit)_3]$ (1) (- - - -), and $[NiCp_2][V(dmit)_3]$ (4) (— · —).

TABLE 3. Electrical conductivities (σ)

Complex	$\sigma_{25\,°C}$ (S cm^{-1})
$[NBu^n_4]_2[V(dmit)_3]$	4.5×10^{-10}
1	1.2×10^{-5}
2	2.5×10^{-6}
3	4.9×10^{-7}
4	4.7×10^{-4}
5	6.9×10^{-5}
6	1.0×10^{-4}

900 nm. This is due to more suitable molecular interaction, as is reflected in its electrical conductivity. The other oxidized $V(dmit)_3$ complexes have exhibited broad bands around 800 nm, indicating molecular interactions through sulfur–sulfur contacts as observed for dmit–metal complexes such as $[epy]_2[Cu(dmit)_2]I_{2.9}$ (epy = *N*-ethylpyridinium) [16] and [Pt(dmit)(bipym)] and [Pt(dmit)(bipym)]I_x (x = 1.6 and 2.7; bipym = 2,2′-bipyrimidine) [17].

Electrical Conductivities

The temperature dependence of the electrical resistivities of compacted pellets has indicated that all the complexes behave as typical semiconductors in the −30 to 25 °C range. Table 3 summarizes the electrical conductivities at 25 °C. Although $[NBu^n_4]_2$-$[V(dmit)_3]$ exhibits a very small conductivity, all the oxidized complexes exhibit an appreciable increase in conductivities. The electrical conduction of these oxidized $V(dmit)_3$ complexes is likely to occur through conduction pathways constructed with sulfur–sulfur contacts of the dmit ligands, as was reported for the crystal structure of $[NMP]_2$-$[V(dmit)_3]$ (NMP = *N*-methylphenazinium) [7].

For complexes **1**, **2** and **4** having the metallocenium cations with similar bulkiness, the degree of charge transfer from the $V(dmit)_3$ moieties to the cations reflects in their conductivities; transfer of more negative charges causes more suitable interactions among the oxidized $V(dmit)_3$ moieties leading to higher electrical conduction. The low conductivity of complex **3** may come from an ineffective packing of the $[V(dmit)_3]^-$ anions owing to bulky configuration of the cation.

Oxidized $V(dmit)_3$ anion complexes with small cations may exhibit high conductivities, as recently reported for $K_{0.4}[Ni(dmit)_2]$ which is metallic down to 20 K [18]. Although complexes **5** and **6** contain Fe^{2+} and Co^+ cations, respectively, the cations are hydrated, the conductivities being limited in 1.0×10^{-4} and 6.9×10^{-5} S cm^{-1}.

Acknowledgements

This work was partially supported by a Grant-in-Aid for scientific research (No. 63540486) from the Ministry of Education, Science and Culture and by a grant of the Material Science Research Foundation.

References

1 J. M. Williams, H. H. Wang, T. J. Emge, U. Geiser, M. A. Beno, P. C. W. Leung, K. D. Carlson, R. J. Thorn and A. J. Schultz, *Prog. Inorg. Chem., 35* (1987) 51.
2 L. Valade, J. P. Legos, M. Bousseau, P. Cassoux, M. Garbauskas and L. V. Interrante, *J. Chem. Soc., Dalton Trans.*, (1985) 783.
3 M. Bousseau, L. Valade, J. P. Legros, P. Cassoux, M. Garbauskas and L. V. Interrante, *J. Am. Chem. Soc., 108* (1986) 1908, and refs. therein.
4 A. Kobayashi, H. Kim, Y. Sasaki, R. Kato, H. Kobayashi, S. Moriyama, Y. Nishio, K. Kajita and W. Sasaki, *Chem. Lett.*, (1987) 1819.
5 L. Brossard, H. Hurdequint, M. Ribault, L. Valade, J. P. Legros and P. Cassoux, *Synth. Met., 27* (1988) B157.
6 J. R. Ferraro and J. M. Williams, *Introduction to Synthetic Electrical Conductors*, Academic Press, New York, 1987.
7 G. Matsubayashi, K. Akiba and T. Tanaka, *Inorg. Chem., 27* (1988) 4744.
8 G. Steimecke, H.-J. Sieler, R. Krimse and E. Hoyer, *Phosphorus and Sulfur, 7* (1979) 49.
9 A. A. Bakke, W. L. Jolly, B. L. Pinsky and J. C. Smart, *Inorg. Chem., 18* (1979) 1343.
10 K. Ueyama, G. Matsubayashi and T. Tanaka, *Inorg. Chim. Acta, 87* (1984) 143.
11 G. Matsubayashi, K. Kondo and T. Tanaka, *Inorg. Chim. Acta, 69* (1983) 167.
12 T. Nojo, G. Matsubayashi and T. Tanaka, *Inorg. Chim. Acta, 159* (1989) 49.
13 J. W. Diggle and A. J. Parker, *Electrochim. Acta, 18* (1973) 975.
14 Y. Sakamoto, G. Matsubayashi and T. Tanaka, *Inorg. Chim. Acta, 113* (1986) 137.
15 A. Horsfield and A. Wassermann, *J. Chem. Soc. A*, (1970) 3202.
16 G. Matsubayashi, K. Takahashi and T. Tanaka, *J. Chem. Soc., Dalton Trans.*, (1988) 967.
17 G. Matsubayashi, Y. Yamaguchi and T. Tanaka, *J. Chem. Soc., Dalton Trans.*, (1988) 2215.
18 A. Clark, A. E. Underhill, I. D. Parker and R. H. Friend, *J. Chem. Soc., Chem. Commun.*, (1989) 228.