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Synthesis, Crystal Structure, and Magnetic Property of a Dinuclear Oxovanadium(IV) Complex with 2,6-Bis(salicylideneaminomethyl)-4-methylphenol

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A dinuclear oxovanadium(IV) complex with 2,6-bis(salicylideneaminomethyl)-4-methylphenol (H_3L), $[(VO)_2(L)(CH_3O)(dmso)]$ (**1**) (dmso = dimethyl sulfoxide), has been synthesized and characterized by infrared and electronic spectra, and by the temperature dependence of magnetic susceptibilities (80—300 K). The molecular structure of **1** was determined by single-crystal X-ray structure analysis. The two octahedral vanadium ions are bridged by a phenoxo-oxygen of L, a methoxo ion, and a dimethyl sulfoxide and have *syn* oxo configuration. The magnetic property was discussed in relation to the crystal structure.

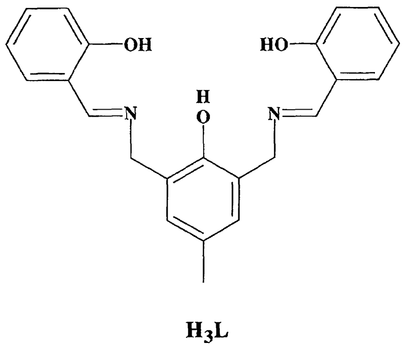
Since an oxovanadium(IV) ion has one d electron, magnetic properties of dinuclear oxovanadium(IV) complexes are of interest to compare with those of dinuclear copper(II) complexes which have also only one unpaired electron in each of their 3d-shells. Unlike the related copper(II) systems, oxovanadium(IV) ion has d_{xy} orbital as the magnetic orbital which can lead to direct overlap as the primary path for magnetic coupling.[1,2] In 1974, Okawa et al. prepared a series of dinuclear oxovanadium(IV) and copper(II) complexes by using Schiff-base ligands, 2,6-bis[*N*-(2-hydroxy-5-substitutedphenyl)iminomethyl]-4-methylphenol, and measured the temperature dependence of the magnetic susceptibilities.[3] They found that the antiferromagnetic spin-exchange interaction in the dinuclear oxovanadium(IV) complexes is generally weak compared with those of the dinuclear copper(II) complexes. However, their dinuclear structures were not confirmed by X-ray structure analysis. So far many oxovanadium(IV) complexes have been reported as dinuclear species, but the literature remains controversial due to the lack of accurate structural information.[1,2] For example, vanadium(IV) complexes with *N*-(hydroxyalkyl)salicylideneamine have been reported by a number of coordination chemists, but considerable controversy surrounded their formulation and magnetic properties since Yamada's first report on these compounds.[4—10] Most of these compounds have been considered to be dimeric oxovanadium(IV). Eventually, 20 years later, Pecoraro et al. have done a conclusive study on this system by giving the first X-ray crystallographic structural data for these oxovanadium(IV) complexes.[11] Therefore X-ray crystallographic characterization is important in vanadium chemistry. Nevertheless, the structural chemistry of dinuclear oxovanadium(IV) complexes has received surprisingly little attention in the past. Only a limited number of dinuclear complexes have been synthesized and characterized by X-ray crystallography.[11—24] We have therefore continued studying structures and magnetic properties of vanadium complexes.[25,26] Herein we report our findings on an oxovanadium(IV) complex of a dinucleating ligand, 2,6-bis(salicylideneaminomethyl)-4-methylphenol, H_3L (Chart 1).

Experimental

Synthesis of the Complex. 2,6-Bis(salicylideneaminomethyl)-4-methylphenol was synthesized according to a method reported by Mezurek et al.[27]

$[(VO)_2(L)(CH_3O)(dmso)]$ (1). To a methanol–dimethyl sulfoxide (1 : 1) solution (6 ml) of H_3L (19 mg, 0.05 mmol), $VOSO_4 \cdot 3H_2O$ (35 mg, 0.15 mmol) was added with stirring. The resulting solution was filtered and three drops of $(C_2H_5)_3N$ were added to the filtrate. The solution was left to stand at 5 °C for several days. Dark brown crystals were deposited; they were collected by filtration, washed by methanol, and dried in vacuo over P_2O_5 (yield 16 mg, 50%). Anal. Calcd for $C_{26}H_{28}N_2O_7SV_2$: C, 50.82; H, 4.59; N, 4.56%. Found: C, 50.48; H, 4.68; N, 4.46%. IR (KBr) ν/cm^{-1} ν(C=N) 1635 (s), ν(V=O) 986 (s), ν(S=O) 956 (s).

Measurements. Carbon, hydrogen, and nitrogen analyses were carried out using a Perkin-Elmer 2400 Series II CHNS/O Analyzer. Infrared spectra were measured with a JASCO Infrared Spectrometer model IR700 in the 4000—400 cm^{-1} region on a KBr



H_3L

Chart 1.

disk. Electronic spectra were measured with a Shimadzu UV-vis-NIR Recording Spectrophotometer Model UV-3100. The magnetic susceptibilities were measured over the 80—300 K temperature range. The susceptibilities were corrected for the diamagnetism of the constituent atoms using Pascal's constants.[28] The effective magnetic moments were calculated from the equation $\mu_{\mathrm{eff}}=2.828\sqrt{\chi_{\mathrm{A}}T}$, where χ_{A} is the atomic magnetic susceptibility.

X-Ray Crystal Structure Analysis of 1. The unit-cell parameters and intensities were measured on an Enraf–Nonius CAD4 diffractometer using graphite-monochromated Mo $K\alpha$ radiation at 25±1°C. The unit-cell parameters were determined by a least-squares refinement based on 25 reflections with $20\leq 2\theta \leq 30°$. Intensity data were collected by the ω–2θ scan technique and corrected for Lorenz-polarization effects, but not for absorption.

Crystal Data: [(VO)$_2$(L)(CH$_3$O)(dmso)] (**1**): $C_{26}H_{28}N_2O_7SV_2$, F.W. = 614.47, Triclinic, $P\bar{1}$, $a=12.475(6)$, $b=12.564(6)$, $c=8.631(3)$ Å, $\alpha=96.15(3)$, $\beta=100.26(3)$, $\gamma=92.05(3)°$, $V=1323(1)$ Å^3, $D_{\mathrm{m}}=1.51$, $D_{\mathrm{c}}=1.54$ g cm^{-3}, $Z=2$, $\mu(\mathrm{Mo}\,K\alpha)=8.05$ cm^{-1}. Specimen: dark brown crystal 0.65×0.50×0.28 mm. A total of 4157 reflections were measured in the range $1\leq 2\theta \leq 48°$; 3391 reflections with $I\geq 3\sigma(\mathrm{I})$ were assumed as observed. $R=0.031$, $R_{\mathrm{w}}=0.033$.

The structure was solved by the direct methods and refined by the full-matrix least-squares method. All the non-hydrogen atoms were refined with anisotropic thermal parameters. The hydrogen atoms were inserted at their calculated positions and fixed at these positions. The weighting scheme, $w=1/[\sigma^2(|F_{\mathrm{o}}|)+(0.02|F_{\mathrm{o}}|)^2+1.0]$, was employed.

All of the calculations were carried out on a VAX station 4000 90A computer using a MolEN program package.[29] The atomic coordinates and thermal parameters of the non-hydrogen atoms are listed in Table 1. The anisotropic thermal parameters of the non-hydrogen atoms, the atomic coordinates and temperature factors of the hydrogen atoms, and the $F_{\mathrm{o}}-F_{\mathrm{c}}$ tables were deposited as Document No. 69012 at the Office of the Editor of Bull. Chem. Soc. Jpn.

Table 1. Fractional Positional Parameters and Thermal Parameters of Non-Hydrogen Atoms with Their Estimated Standard Deviations in Parentheses

Atom	x	y	z	B_{eq}/Å^2 [a)]
V1	0.61646(4)	0.20104(4)	0.41421(6)	2.94(1)
V2	0.78003(4)	0.37802(4)	0.44932(6)	2.61(1)
S1	0.75789(7)	0.35239(7)	0.85585(9)	3.59(2)
O1	0.4836(2)	0.2368(2)	0.4955(3)	3.99(5)
O2	0.7830(2)	0.2126(2)	0.4460(2)	2.68(4)
O3	0.7526(2)	0.5201(2)	0.5455(3)	3.62(5)
O4	0.5822(2)	0.1363(2)	0.2455(3)	4.82(6)
O5	0.8186(2)	0.3970(2)	0.2880(3)	4.07(5)
O6	0.6255(2)	0.3497(2)	0.3742(2)	3.03(4)
O7	0.7134(2)	0.3243(2)	0.6834(2)	4.12(5)
N1	0.6366(2)	0.0768(2)	0.5531(3)	2.90(5)
N2	0.9328(2)	0.3837(2)	0.5858(3)	2.66(5)
C1	0.8590(2)	0.1534(2)	0.5384(3)	2.58(6)
C2	0.9655(2)	0.1907(2)	0.5910(3)	2.72(6)
C3	1.0407(2)	0.1309(3)	0.6865(4)	3.13(6)
C4	1.0161(3)	0.0337(3)	0.7323(4)	3.29(7)
C5	0.9120(3)	−0.0033(2)	0.6755(4)	3.20(6)
C6	0.8341(3)	0.0532(2)	0.5793(3)	2.89(6)
C7	1.0992(3)	−0.0294(3)	0.8371(4)	4.56(8)
C8	0.7245(3)	0.0025(2)	0.5191(4)	3.48(7)
C9	0.5846(3)	0.0614(2)	0.6642(4)	3.24(6)
C10	0.5013(2)	0.1314(2)	0.7146(4)	3.19(6)
C11	0.4677(3)	0.1159(3)	0.8571(4)	4.75(8)
C12	0.3918(3)	0.1815(4)	0.9155(5)	5.7(1)
C13	0.3441(3)	0.2630(3)	0.8295(5)	5.05(9)
C14	0.3737(3)	0.2805(3)	0.6892(4)	4.12(8)
C15	0.4548(2)	0.2163(2)	0.6291(4)	3.23(7)
C16	1.0025(2)	0.2927(3)	0.5431(4)	3.28(7)
C17	0.9714(2)	0.4569(2)	0.6937(4)	2.91(6)
C18	0.9135(2)	0.5517(2)	0.7429(3)	2.83(6)
C19	0.9666(3)	0.6204(3)	0.8705(4)	3.72(7)
C20	0.9197(3)	0.7151(3)	0.9206(4)	4.50(8)
C21	0.8181(3)	0.7436(3)	0.8422(4)	4.41(8)
C22	0.7631(3)	0.6786(3)	0.7173(4)	3.66(7)
C23	0.8085(2)	0.5803(2)	0.6646(4)	2.92(6)
C24	0.5399(3)	0.4193(3)	0.3220(4)	4.43(8)
C25	0.6545(4)	0.4248(5)	0.9351(5)	9.3(1)
C26	0.7578(4)	0.2354(3)	0.9493(5)	6.1(1)

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

Results and Discussion

In recent reports, we described the synthesis and characterization of the related other metal complexes with 2,6-bis(salicylideneaminomethyl)-4-methylphenol, H$_3$L.[30—33] In these cases, we obtained dinuclear Ni(II), tetranuclear Ni(II), tetranuclear Mn(III), and pentanuclear Fe(III) complexes. On the other hand, in the case of oxovanadium(IV), a dinuclear species **1** could be prepared in methanol–dimethyl sulfoxide by using VOSO$_4$ as the vanadium source. The bent structure with the "*anti*" configuration of **1** (vide infra) seems to prevent further association of the dinuclear units into oligonuclear structures found in the other metal complexes with this ligand.[30—33] Dimethyl sulfoxide was essential to get good crystals suitable for a single-crystal X-ray diffraction study. The X-ray crystal structure of **1** has been determined. A perspective drawing of the molecular structure of **1** is given in Fig. 1. Selected bond distances and angles are listed in Table 2. The two vanadium atoms with terminal oxo groups, V1 and V2, are bridged by a phenoxo-oxygen (O2) of L, a methoxo-oxygen (O6), and an oxygen atom (O7) of dimethyl sulfoxide, forming a distorted octahedral environment for each metal center. The V1–V2 separation is 3.026(1) Å and the V1–O2–V2 and V1–O6–V2 angles are 94.3(1) and 101.8(1)°, respectively. The terminal oxo-groups are in *syn*-positions with respect to each other. The V1–O4 [1.586(2) Å] and V2–O5 [1.595(2) Å] bond lengths are short and indicates considerable double bond character, as is usual for vanadyl compounds.[2] In the IR spectrum of **1**, the V=O stretching band was observed at 986 cm^{-1}, which is within the range [935—1035 cm^{-1}] expected for a simple oxovanadium(IV) species.[34] The two vanadium atoms are further bridged by an oxygen atom (O7) of dimethyl sulfoxide. The bridging of dimethyl sulfoxide is evident from the shift to a lower frequency of the S=O stretching band (956 cm^{-1}) in the IR spectrum of **1**.[35] The V1–O7 [2.761(2) Å] and V2–O7 [2.481(2) Å] bond distances trans to the V=O groups are significantly longer than the other equatorial V–O distances

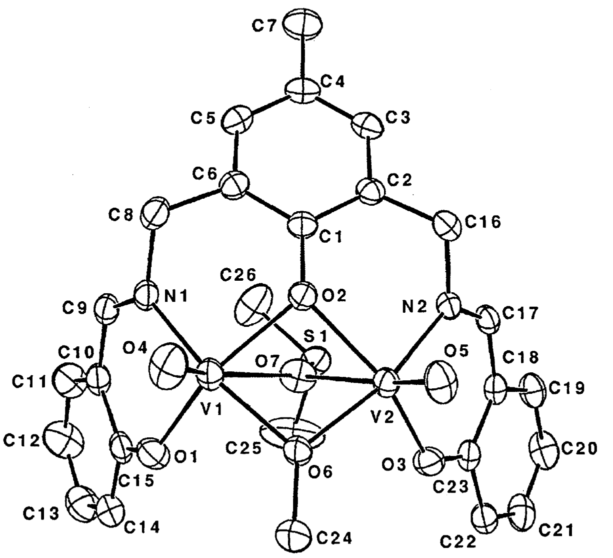


Fig. 1. A perspective view of the structure of **1**, showing the atom-labeling scheme. Thermal ellipsoids are at the 35% probability level.

[1.932(2)—2.074(2) Å]. In the least-square plane defined by N1, O1, O6, and O2 atoms, V1 atom is displaced towards the terminal oxygen by 0.49 Å. Similarly, V2 atom is displaced in the same direction from the O2–O6–O3–N2 mean plane by 0.39 Å. The dihedral angle between these two planes (τ) is 131.1°. As shown in Fig. 2, the dinucleating ligand takes a roof-shaped structure, the dihedral angle between the two salicylideneamino moieties being 70.7°. It is noteworthy that the dimethyl sulfoxide molecule is incorporated in this cavity.

Table 2. Selected Interatomic Distances (l/Å) and Bond Angles (ϕ/°) with Their Estimated Standard Deviations in Parentheses

V1–V2	3.0264(7)	V2–O2	2.074(2)
V1–O1	1.933(2)	V2–O3	1.932(2)
V1–O2	2.055(2)	V2–O5	1.595(2)
V1–O4	1.586(2)	V2–O6	1.954(2)
V1–O6	1.946(2)	V2–O7	2.481(2)
V1–O7	2.761(2)	V2–N2	2.054(2)
V1–N1	2.050(3)		
O1–V1–O2	147.88(8)	O2–V2–O3	151.93(9)
O1–V1–O4	106.7(1)	O2–V2–O5	103.5(1)
O1–V1–O6	89.04(9)	O2–V2–O6	80.36(8)
O1–V1–O7	84.00(8)	O2–V2–O7	69.49(8)
O1–V1–N1	87.1(1)	O2–V2–N2	89.86(8)
O2–V1–O4	105.3(1)	O3–V2–O5	104.6(1)
O2–V1–O6	81.04(8)	O3–V2–O6	93.52(8)
O2–V1–O7	63.91(7)	O3–V2–O7	82.44(9)
O2–V1–N1	88.90(9)	O3–V2–N2	88.08(9)
O4–V1–O6	105.7(1)	O5–V2–O6	100.9(1)
O4–V1–O7	168.2(1)	O5–V2–O7	172.4(1)
O4–V1–N1	99.7(1)	O5–V2–N2	95.9(1)
O6–V1–O7	68.90(7)	O6–V2–O7	75.46(8)
O6–V1–N1	154.35(9)	O6–V2–N2	162.1(1)
O7–V1–N1	85.48(8)	O7–V2–N2	87.11(9)
V1–O2–V2	94.27(8)	V1–O7–V2	70.30(5)
V1–O6–V2	101.79(9)		

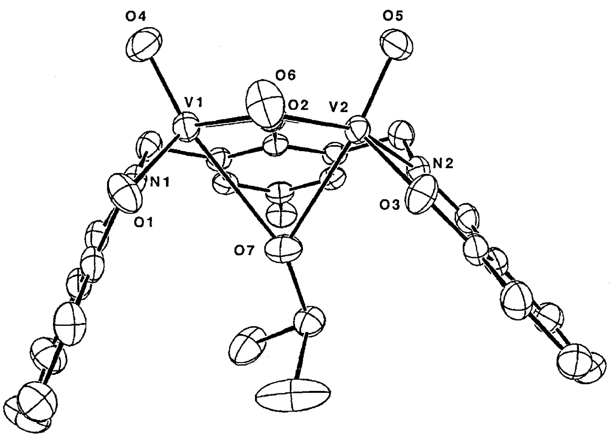


Fig. 2. Another view of the structure of **1**. Thermal ellipsoids are at the 35% probability level.

The diffuse reflectance spectrum of **1** is shown in Fig. 3. The spectrum is characterized by three absorptions (484sh, 547sh, and 721 nm) in the visible region, which can be associated with d–d transitions and intense absorptions in the range 250—400 nm; these (284 and 369 nm) are charge-transfer transitions in origin. The three absorption bands at 484, 547, and 721 nm may be assigned as $^2B_2\rightarrow{}^2A_1$, $^2B_2\rightarrow{}^2B_1$, and $^2B_2\rightarrow{}^2E$ transitions, respectively.[36)]

The temperature dependence of the magnetic susceptibilities of **1** was measured in the temperature range 80—300 K (Fig. 4). The magnetic moment of **1** is 2.02 B.M. per dinuclear molecule at 299 K, which is lower than the spin-only value (2.45 B.M.) for two uncoupled $S=1/2$ spins, and gradually decreases on decreasing temperature, reaching 0.59 B.M. at 80 K. For the analysis of the magnetic susceptibility data, we employed the $S=1/2-S=1/2$ system based on the Heisenberg model $\mathscr{H}=-2JS\cdot S$. The resulting magnetic susceptibility expression in given by

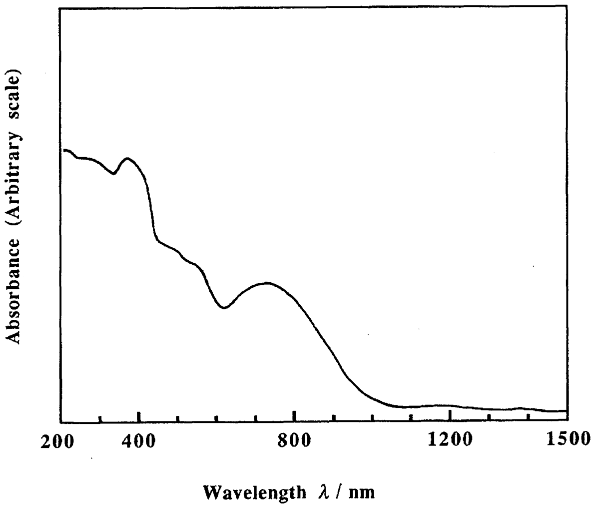


Fig. 3. Diffuse reflectance spectrum of **1**.

Table 3. Magnetic and Structural Parameters for Phenoxo- or Hydroxo-Bridged Dinuclear Oxovanadium(IV) Complexes

Complex	J/cm^{-1}	$R^{d)}$/Å	$\theta^{e)}$/°	$\tau^{f)}$/°	Ref.
$[(VO)_2(L)(OCH_3)(dmso)]$ (**1**)	−122	3.026	94.3, 101.8	131.1	This work
$[(VO)_2(L^1)(SO_4)]\cdot CH_3OH\cdot 3H_2O$ [a] (**2**)	−128	3.077	99.4	150.1	23
$[(VO)_2(L^2)(OH)_2]I_2\cdot 4H_2O$ [b] (**3**)	−150	2.965	98.1	175.7	18
$[(VO)_2(L^3)(OH)_2]Br_2$ [c] (**4**)	−177	3.033	101.2	180.0	17

a) L^1 = Macrocyclic ligand containing 2,6-bis(*N*-alkylamino)phenol units. b) L^2 = *N*,*N*,*N*′,*N*′-Tetrakis(2-pyridylmethyl)ethylenediamine. c) L^3 = 1,4,7 − Triazacyclononane. d) V–V separation. e) V–O–V angle. f) Dihedral angle between the coordination planes.

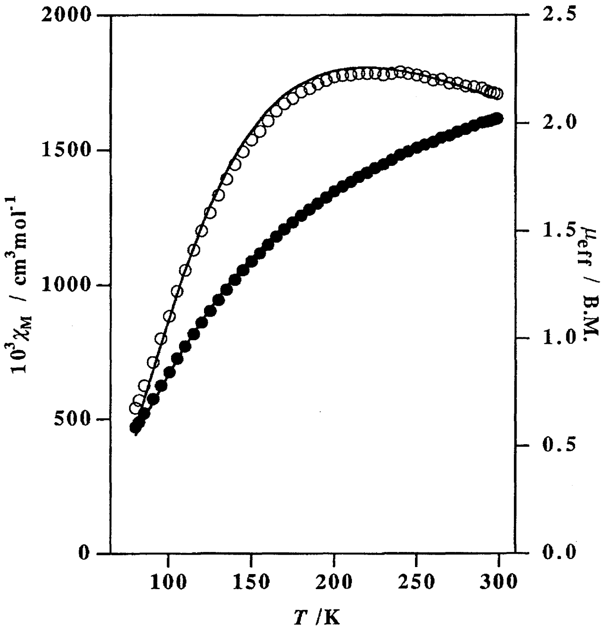


Fig. 4. Magnetic susceptibilities (○) and effective magnetic moments (●) of **1**.

$$\chi_M = \frac{2Ng^2\beta^2}{kT}\left[\frac{1}{3+\exp(-2J/kT)}\right].$$

The symbols N, β, k, and g have their usual meanings. The best fitting parameters are g=2.05 and J=−122 cm^{-1}; the solid curve in Fig. 4 was calculated using these parameters. This result shows that there is an significant antiferromagnetic interaction between the two vanadium(IV) ions. In dinuclear oxovanadium(IV) complexes, a direct overlap of d_{xy} orbitals is considered as the dominant magnetic exchange pathway. An alternative superexchange pathway of $d_{x^2-y^2}$, which is dominant for dinuclear copper(II) complexes, is thought to be negligible. In spite of a large number of oxovanadium(IV) complexes showing antiferromagnetic interaction, no structure–magnetic property correlation is elucidated for dinuclear oxovanadium(IV) complexes because of the paucity of structural data. In Table 3, the magnetic data and the structural parameters for phenoxo- or hydroxo-bridged dinuclear oxovanadium(IV) complexes are collected.[17,18,23] The J values vary from −122 to −177 cm^{-1}, while the V–V separation has almost identical values, lying between 2.965 and 3.077 Å. The V–O–V angle has

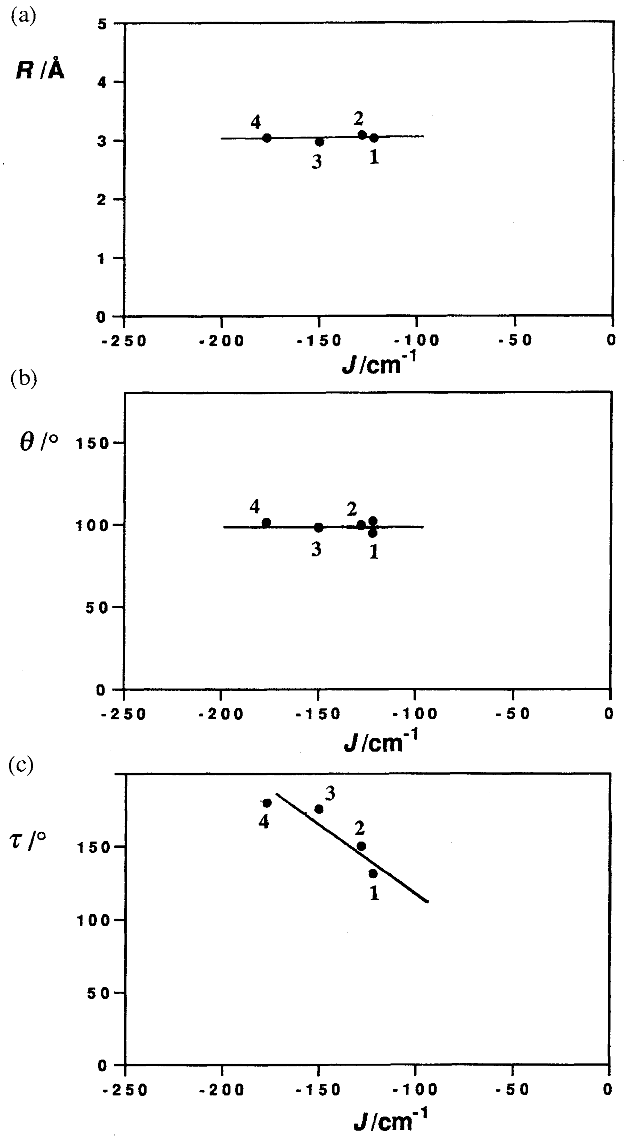


Fig. 5. The relationship between the magnetic data and the structural parameters of phenoxo- or hydroxo-bridged dinuclear oxovanadium(IV) complexes. Top: A plot of the J value vs. the V–V separation, R. Middle: A plot of the J value vs. the V–O–V angle, θ. Bottom: A plot of the J value vs. the dihedral angle between the coordination planes, τ.

also almost identical values. This means that the variation of J may be caused by other factors than the V–V separation or the V–O–V angle. In Fig. 5, the J values were plotted against the V–V separations (R), the V–O–V angles (θ), and the dihedral angle between the two coordination planes (τ), respectively. As seen in Fig. 5, $-J$ value decreases with decreasing τ. These results reveal that the τ value is the major factor to determine the J value, showing that the major pathway for magnetic coupling is a direct overlap of d_{xy} orbitals in dinuclear oxovanadium(IV) complexes.

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