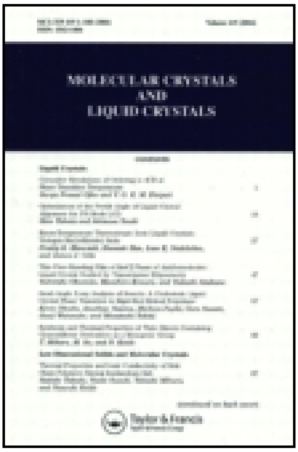

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# Structures and Magnetic Properties of Dinuclear Oxovanadium(IV) Complexes with Tris(μ-diphenylphosphinato)-bridges

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Novel dinuclear oxovanadium(IV) complexes with tris(μ-phosphinato)-bridges, $[(VO)_2(dpp)_3(bpy)_2]NO_3 \cdot 2H_2O$ (**1**), $[(VO)_2(dpp)_3(phen)_2]NO_3 \cdot H_2O$ (**2**) and $[(VO)_2(bmp)_3(bpy)_2]NO_3 \cdot H_2O$ (**3**) (Hdpp = diphenylphosphinic acid, Hbmp = bis(4-methoxyphenyl)phosphinic acid, bpy = 2,2'-bipyridine, phen = 1,10-phenanthroline), have been prepared and structurally characterized by X-ray crystallography. Crystal structures of complexes **1** and **3** have revealed that two vanadium ions in each molecule are linked by tris(μ-phosphinato)-bridges. Magnetic susceptibility data for **1**-**3** conform to the usual dimer equation with the $-2J$ values of 16-21 $cm^{-1}$, indicating weak antiferromagnetic interaction is operative between vanadium(IV) ions.

Keywords dinuclear oxovanadium(IV) complex; phosphinato bridge; crystal structure; magnetic susceptibility; antiferromagnetic interaction

## INTRODUCTION

Many transition metal complexes having a μ-carboxylato-bridged dimetal core have been reported as a structural motif in biology and inorganic chemistry. In our previous study[1], we described both the properties and the crystal structures for novel vanadium(IV) analogues of the hemerythrin active center. As a part of continuing projects on this study, we have prepared novel dinuclear oxovanadium(IV) complexes having tris(μ-phosphinato)-bridges with bidentate terminal ligands such as bpy or phen. Dinuclear oxovanadium(IV) complexes having only phosphinate anions as bridging ligands are still rare. Dean *et al.*[2] obtained dinuclear oxovanadium(IV) complexes with bis(μ-diphenylphosphinato)-bridges, in which tridentate hydrotris(pyrazolyl)borate was used as a terminal ligand for these complexes. On the other hand, to the best of our knowledge no dinuclear oxovanadium(IV) complexes having tris(μ-phosphinato)-bridges with bidentate terminal ligands are known. Here we report the X-ray structural characterization of complexes **1-3** together with their magnetic properties.

## EXPERIMENTAL

### Preparation of Compounds

**[VOCl$_2$X(EtOH)]**.[1, 3] To a solution of $VCl_3$ in EtOH was added the terminal ligand X in EtOH, where X is bpy or phen. An immediate color change to deep violet was observed. After the solution was refluxed for 3 d at 80℃, a precipitated green powder was collected, washed with EtOH, and dried under air (yield 60%).

**[(VO)$_2$L$_3$X$_2$]NO$_3$·nH$_2$O**. L = dpp or bmp (Hdpp = diphenylphosphinic acid, Hbmp = bis(4-methoxyphenyl)-phosphinic acid)
To a green solution of [VOCl$_2$X(EtOH)] (1 mmol) in MeOH (50 mL) was added $AgNO_3$ (1 mmol). The solution was heated and stirred for 5 min with shutting off the light, and the resulting suspension was centrifuged and filtered off. Phosphinic acid HL (2 mmol) was added to the filtrate under stirring, and the reaction mixture was adjusted to pH ≈ 6.0 with triethylamine. The solution was allowed to stand for some days at room temperature. Green crystals were collected, washed with EtOH, and dried under air.
Anal. Calcd for $[(VO)_2(dpp)_3(bpy)_2]NO_3\cdot 2H_2O$ (**1**): C, 56.25; H, 4.22; N, 5.86. Found: C, 55.98; H, 4.45; N, 5.62.
Anal. Calcd for $[(VO)_2(dpp)_3(phen)_2]NO_3\cdot H_2O$ (**2**): C, 58.79; H, 3.95; N, 5.71. Found: C, 58.89; H, 3.90; N, 5.72.
Anal. Calcd for $[(VO)_2(bmp)_3(bpy)_2]NO_3\cdot H_2O$ (**3**): C, 54.84; H, 4.45; N,

5.16. Found: C, 54.58; H, 4.47; N, 5.11.

### Physical Measurements

Elemental C, H, N analyses were obtained at the Service Center of Elemental Analysis at Kyushu University. The magnetic susceptibilities were determined by the Faraday method. The susceptibilities were corrected for the diamagnetism of the constituent atoms using Pascal's constants.[4]

### X-Ray Crystal Structure Determination

The diffraction data were measured on a Rigaku AFC5S automated four-circle diffractometer. The data were collected using the $\omega-2\theta$ scan technique to a maximum $2\theta$ value of 55°. Crystal data and data collections parameters: **1**, $C_{56}H_{50}N_5O_{13}P_3V_2$, $M = 1195.90$, triclinic, $a = 11.760(4)$, $b = 16.883(9)$, $c = 16.787(7)$ Å, $V = 2912(3)$ Å$^3$, space group $P\bar{1}$(#2), $Z = 2$, $\mu$(Mo-K$\alpha$) = 4.718cm$^{-1}$, 2943 reflections measured, 681 unique reflections with $I > 3.00\sigma(I)$. Final value for $R = 0.074$ / $R_w = 0.082$: **3**, $C_{62}H_{60}N_5O_{18}P_3V_2$, $M = 1357.98$, triclinic, $a = 14.66(4)$, $b = 18.88(1)$, $c = 12.69(1)$ Å, $V = 3156(10)$ Å$^3$, space group $P\bar{1}$(#2), $Z = 2$, $\mu$(Mo-K$\alpha$) = 4.474cm$^{-1}$, 3412 reflections measured, 580 unique reflections with $I > 3.00\sigma(I)$. Final value for $R = 0.120$ / $R_w = 0.175$

## RESULTS AND DISCUSSION

The crystal structures of **1** and **3** are shown in Figures 1 (a) and (b). The complexes are consisted of a dioxovanadium core with two hexacoordinated vanadium ions linked by tris(μ-phosphinato)-bridges. The coordination environment around each vanadium ion is a distorted octahedral geometry with the equatorial plane comprised of two nitrogen atoms of a terminal ligand, and two oxygen atoms of two bridging ligands. The axial sites are occupied by oxygen atoms of the oxovanadium group and of another bridging phosphinato group. The V···V separation and the dihedral angle of equatorial planes of **1** and **3** are 4.87(2) Å, 130° , and 4.87(1) Å, 80° , respectively. Two POO groups in **1** connect each vanadium center at equatorial-axial sites and another one bridges at equatorial-equatorial sites. In **3**, however, two POO groups connect each vanadium center at equatorial-equatorial sites and another one forms an axial-axial bond.

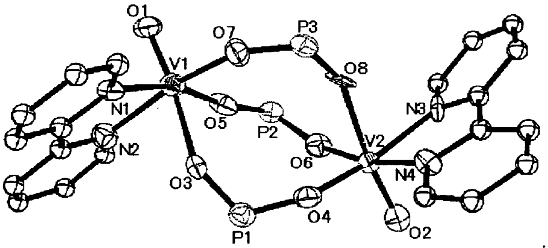

FIGURE 1(a) An ORTEP drawing of the cation for **1**.
*Phenyl groups of bridging ligands were omitted for clarity.
Selected bond lengths(Å): V1···V2 4.87(2), V1-O1 1.55(3), V1-O3 2.12(3), V1-O5 1.99(3), V1-O7 1.99(2), V1-N1 2.12(3), V1-N2 2.10(4), V2-O2 1.58(3), V2-O4 1.97(2), V2-O6 2.07(2), V2-O8 2.17(8), V2-N3 2.17(3), V2-N4 2.10(3)

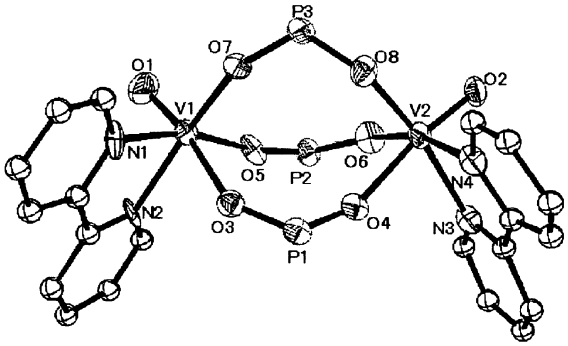

FIGURE 1(b) An ORTEP drawing of the cation for **3**.
*Phenyl groups of bridging ligands were omitted for clarity.
Selected bond lengths(Å): V1···V2 4.87(1), V1-O1 1.60(2), V1-O3 2.13(2), V1-O5 2.03(2), V1-O7 2.02(2), V1-N1 2.19(2), V1-N2 2.13(2), V2-O2 1.59(2), V2-O4 2.14(2), V2-O6 1.97(2), V2-O8 2.00(2), V2-N3 2.20(2), V2-N4 2.18(2)

The magnetic properties of the present complexes were measured in the temperature range of 80–300 K. Plots of the magnetic susceptibilities are shown in Figure 2. The analysis was carried using a modified equation (1) for the dinuclear cluster of vanadium(IV) ions ($S_1 = S_2 = 1/2$). The best fitting parameters obtained by a non-linear least-square method are listed in Table 1. The values of $-2J$ show very weak antiferromagnetic behavior exists in **1**-**3**. For **1** the effective magnetic moment ($\mu_{eff}$) per one vanadium center decreases slightly from 1.79 B.M. at 298.8 K to 1.75 B.M. at 81.2 K. Complexes **2** and **3** show analogous magnetic behavior to that of **1**. Each unpaired electron in binuclear oxovanadium(IV) complexes having an octahedral configuration generally resides in a $d_{xy}$ orbital with the oxo group oriented along the z direction. Dihedral angles of two vanadium centers for **1**-**3** become large by phosphinato bridging. Then superexchange pathways *via* $d_{x^2-y^2}$ are thought to be negligible. For relatively weak antiferromagnetic coupling of the present complexes, a through space direct overlap[3] of the $d_{xy}$ orbitals is predominant.

$$\chi_A = \left(\frac{N\beta^2 g^2}{kT}\right)\left[3+\exp\left(\frac{-2J}{kT}\right)\right]^{-1}(1-p)+\left(\frac{N\beta^2 g_i^{\,2}}{4kT}\right)p+N\alpha \qquad (1)$$

$$\mu_{eff} = 2.83\sqrt{(\chi_A - N\alpha)T}$$

TABLE 1. Magnetic Data for Complexes **1-3**

| Complex | $-2J$ / cm$^{-1}$ | g | $N\alpha$ / $10^{-6}$cm$^3$mol$^{-1}$ | p / % | $\sigma_{dis}$ / % | $\mu_{eff}$ / B.M. (T / K) |
|---|---|---|---|---|---|---|
| **1** | 17 | 2.11 | 60 | 0 | 1.02 | 1.79 (298.8) |
| **2** | 16 | 2.05 | 60 | 0 | 0.85 | 1.75 (299.0) |
| **3** | 21 | 2.03 | 60 | 0 | 0.72 | 1.72 (299.4) |

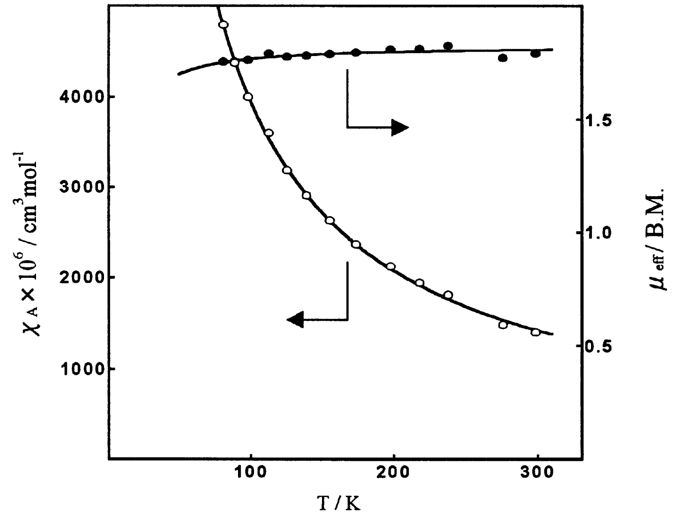

FIGURE 2. Temperature dependence of magnetic susceptibilities $\chi_A$(○) and effective magnetic moments $\mu_{eff}$(●) for **1**.

## CONCLUSION

Novel dinuclear oxovanadium(IV) complexes with tris(μ-diphenylphosphinato)-bridges have been prepared. The −2J values of 16-21 cm$^{-1}$ for **1-3** indicate that a weak antiferromagnetic interaction is operative between vanadium(IV) ions. A through space direct overlap[3] of the $d_{xy}$ orbitals is predominant for this weak magnetic coupling in the present complexes.

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