*Polish J. Chem.*, **75**, 1695–1701 (2001)

# Synthesis, Crystal Structure and Magnetism of Vanadium(IV/V) Complex: $K_3[V_2O_3(nta)_2]\cdot3H_2O$

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*(Received March 15th, 2001; revised manuscript June 25th, 2001)*

The crystal of the titled vanadium(IV/V) complex $K_3[V_2O_3(nta)_2]\cdot3H_2O$ (nta denotes nitrilotriacetate) has been synthesized and its structure determined. The unit cell contains two different binuclear vanadium(IV/V) groups. The vanadium(IV/V) ions are coordinated by six atoms and each vanadium(IV/V) ion is located in the sphere of distorted octahedral coordination. In each dimer two vanadium ions are in exact equivalent sites and one free electron is shared equally between the two vanadium ions.

**Key words:** complex synthesis, magnetism, crystal structure

The study of vanadium complexes is of current interest for they play an important role in bioinorganic chemistry, geochemistry, sol-gel chemistry, as well as for catalysis and materials science [1–7]. The present complex belongs to the type complexes [8–9] that binuclear mixed valence vanadium(IV/V) ions are in symmetrical and equivalent sites, and the free electron is shared equally between the two vanadium(IV/V) ions. Although the present complex has the same ligand and a similar coordination sphere with that of complex $(NH_4)_3[V_2O_3(nta)_2]\cdot3H_2O$ [8], the presented synthetic method is different from that of the complex $(NH_4)_3[V_2O_3(nta)_2]\cdot3H_2O$ [8] and the crystal structure is not the same with that of the complex $(NH_4)_3[V_2O_3(nta)_2]\cdot3H_2O$. In addition, we determined the magnetism of the present complex at 4 ~ 300 K in order to understand the magnetic property of the complexes of this category. Here we report the synthesis, the crystal structure and the magnetism of the present complex.

## EXPERIMENTAL

**Materials:** All the starting materials were of analytical grade.
**Preparation of the complex:** $V_2O_5$ (0.4729 g, 2.6 $10^{-3}$ mol), KOH (0.4994 g, 8.9 $10^{-3}$ mol), nitrilotriacetic acid (1.7713 g, 1.0 $10^{-2}$ mol) and $H_2O$ (20 $cm^3$ ) were mixed, heated and stirred at 60°C for *ca.* 10 hours. Then the mixture was filtered and the filtrate was kept at room temperature for 25 days the deep black-blue single crystal appeared and it was used for the physical measurements.
**Physical measurements:** Analysis for C, H and N were performed on a Perkin-Elmer analyser, Model 240, the vanadium content was determined on a PE-ICP 1000. The IR spectrum was recorded with a Perkin-Elmer 783 IR spectrophotometer on a KBr disc, the electronic reflection spectrum and ESR spec-

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trum was recorded using a UV-3100 spectrophotometer and ER-200D-SRC magnetic resonance spectrometer, respectively. The magnetic moments were measured on a magnetic property measurement system, Model MPMS-7.

**Crystallographic data:** $C_{12}H_{18}K_3N_2O_{19}V_2$: Mr = 713.46, monoclinic, space group $P2_1/c$, $a = 17.456(4)$, $b = 9.779(2)$ and $c = 14.889(3)$ Å; $\beta = 107.03(3)°$, $V = 2430.1(9)$ Å$^3$, $Z = 4$, $D_{calc} = 1.950$ g·cm$^{-3}$. A deep black-blue crystal having approximate dimensions of 0.50  0.42  0.36 mm was mounted on a glass fiber. The determination of unit cell and data collection was performed with Mo*Kα* radiation ($\lambda = 0.71073$ Å) on a Siemens P4 4-circle diffractometer equipped with a graphite crystal monochromator. A total of 5591 independent reflections were collected in the range of $2.41° \leq \theta \leq 25.00°$ by ω-2θ scan technique at room temperature (20 ± 2°C), in which 4275 ($R_{int} = 0.0135$ ) reflections with $I \geq 3\sigma(I)$ were considered to be observed and used the succeeding refinements. The correction for $L_p$ factors was applied to the data and the refinement methods are based on full-matrix least-squares on $F^2$. The final $R$ indices [$I > 2\sigma$] are 0.0458 and 0.1476 for conventional factor $R$ and weighted $R$ factor $wR$, respectively. The goodness-of-fit value on $F^2$ is 0.701. The highest peak on the final difference fourier map had a height of $P_{min} = -0.499$ eÅ$^{-3}$ and $P_{max} = 0.898$ eÅ$^{-3}$. All calculation was performed by using SHELXTL-PLUS program system.

## RESULTS AND DISCUSSION

**General characterization:** The result of the elemental analysis is consistent with that of the crystal structure $\{K_3[V_2O_3(nta)_2]\ 3H_2O\}$ (V, 13.86; C, 20.98; H, 2.60; N, 3.65% for measurement; V, 14.28; C, 20.20; H, 2.54; N, 3.93% for calcd.). The IR spectrum exhibits strong bands at 1640 cm$^{-1}$ and 1370 cm$^{-1}$, which may be attributed to the carboxylato groups $\nu_{as}$ and $\nu_s$, respectively. The value of $\nu_{as} - \nu_s$ suggests that the carboxylato groups of nitrilotriacetate coordinated the vanadium(IV/V) in the unidentate. The strong band at 920 cm$^{-1}$ obviously comes from the vibration absorption of terminal V=O bond [9], and the band at 740 cm$^{-1}$ may be attributed to the vibration of V–O–V bonds [11]. In addition, the strong and broad band at 3400 cm$^{-1}$ indicates that there exists $H_2O$ in the complex. All the assignments of IR results are consistent with the results of the crystal structure measurement. The electronic reflectance spectrum exhibits a weak band at *ca.* 17240 cm$^{-1}$ and strong bands at 25000 cm$^{-1}$ and above 25000 cm$^{-1}$, and the former may be attributed to the d ~ d transition for vanadium(IV) ions and later for charge transition. The microcrystal ESR spectrum of the complex at X band was recorded at room temperature. Only a band at *ca.* 3530 (G) (g = 1.987) appeared, which indicates that there exist vanadium(IV) ions in the complex.

**Crystal structure of the complex:** Atomic coordinates, selected bond lengths, and selected bond angles are listed in Table 1, Table 2, Table 3 and Table 4, respectively. The crystal structure with atomic numbering scheme is given in Fig. 1, and the perspective packing diagram of the crystal along b axis is given in Fig. 2. From the Tables and Figures we can know that the terminal V=O distances [1.609(3), 1.611(3) Å] and the V–O (μ-O) bond lengths [1.8085(7) Å, 1.8167(7) Å] are very closed to that of those observed in other mixed valence vanadium(IV/V) complexes [8–9,12–13]. The N–V bond lengths [2.283(3) Å] and the V–O (carboxylate) bond distances [1.976(3) Å, 1.982(3) Å, 2.043(3) Å, 1.970(3) Å, 1.983(3) Å, 2.039(3) Å] are also in the range found for related complexes [8–9,12–13]. From the bond lengths it is obvious that the vanadium(IV/V) ions are in exactly equivalent sites and the free electron must be shared equally between the two vanadium(IV/V) ions in each binuclear units. From the bond lengths and bond angles it is indicated that each vanadium(IV/V) ion locates on a distorted octahedral coordination sphere. Although the radii of $K^+$ ion and $NH_4^+$ ion are very close, the crystal structures for $K_3[V_2O_3(nta)_2]$ $3H_2O$ and $(NH_4)_3[V_2O_3(nta)_2]$ $3H_2O$ belong to different space groups and the present complex contains two different binuclear groups and they are not identical in the bond angles as shown in Table 4. The difference obviously comes from the different balance cations. It may indicate that the minor difference in the balance cations can cause some difference of the crystal structures for vanadium complexes. In addition, the deposit number in CCDC for present complex is 161874.

**Table 1.** Atomic coordinates ($\times 10^{-4}$) and thermal parameters (Å × $10^3$).

| Atom | x | y | z | U(eq) |
|---|---|---|---|---|
| V(1) | 9401(1) | 8417(1) | 4566(1) | 29(1) |
| V(2) | 4507(1) | 3429(1) | 4458(1) | 25(1) |
| K(1) | 7167(1) | 1697(1) | 4986(1) | 47(1) |
| K(2) | 7520(1) | 1256(1) | 7572(1) | 37(1) |
| K(3) | 7576(1) | 6358(2) | 4705(1) | 76(1) |
| O(1) | 9467(2) | 7610(3) | 5500(2) | 48(1) |
| O(2) | 10000 | 10000 | 5000 | 33(1) |
| O(3) | 10462(2) | 7735(3) | 4291(2) | 39(1) |
| O(4) | 11397(2) | 8136(3) | 3581(2) | 50(1) |
| O(5) | 7792(2) | 11247(3) | 3550(2) | 44(1) |
| O(6) | 8448(2) | 9388(3) | 4214(2) | 38(1) |
| O(7) | 8361(2) | 6009(3) | 2316(2) | 56(1) |
| O(8) | 8897(2) | 6865(3) | 3728(2) | 43(1) |
| O(9) | 6412(2) | 3440(4) | 3516(3) | 68(1) |
| O(10) | 5477(2) | 2859(3) | 4163(2) | 36(1) |
| O(11) | 2825(2) | 6318(3) | 3716(2) | 50(1) |
| O(12) | 3457(2) | 4369(3) | 4215(2) | 36(1) |
| O(13) | 3223(2) | 1435(3) | 2101(2) | 48(1) |
| O(14) | 3912(2) | 1992(3) | 3547(2) | 34(1) |
| O(15) | 5000 | 5000 | 5000 | 30(1) |
| O(16) | 4539(2) | 2477(3) | 5378(2) | 42(1) |
| C(1) | 10725(2) | 8348(4) | 3669(3) | 33(1) |
| C(2) | 10173(2) | 9370(4) | 3049(3) | 35(1) |
| C(3) | 8919(2) | 10542(4) | 3080(2) | 28(1) |
| C(4) | 8337(2) | 10416(4) | 3643(3) | 30(1) |
| C(5) | 8856(3) | 8265(4) | 2402(3) | 37(1) |
| C(6) | 8688(2) | 6940(4) | 2831(3) | 35(1) |
| C(7) | 5735(2) | 3595(4) | 3598(3) | 34(1) |

Table 1 (continuation)

| | | | | |
|---|---|---|---|---|
| C(8) | 5187(2) | 4680(4) | 3049(3) | 32(1) |
| C(9) | 3913(2) | 5729(4) | 3138(3) | 28(1) |
| C(10) | 3349(2) | 5478(4) | 3722(3) | 32(1) |
| C(11) | 3890(2) | 3562(4) | 2322(2) | 34(1) |
| C(12) | 3644(2) | 2228(4) | 2665(3) | 29(1) |
| N(1) | 9346(2) | 9236(3) | 3090(2) | 25(1) |
| N(2) | 4357(2) | 4468(3) | 3070(2) | 24(1) |
| Ow1 | 6113(2) | 805(3) | 5982(3) | 62(1) |
| Ow2 | 7415(3) | –1185(4) | 5490(3) | 87(1) |
| Ow3 | 8560(2) | 731(4) | 9464(3) | 84(1) |

**Table 2.** Hydrogen coordinates ( $10^4$ ) and isotropic displacement parameters (Å $10^3$).

| Atom | x | y | z | U(eq) |
|---|---|---|---|---|
| H(2A) | 10364(2) | 10286(4) | 3242(3) | 80 |
| H(2B) | 10181(2) | 9243(4) | 2406(3) | 80 |
| H(3A) | 8633(2) | 10787(4) | 2437(2) | 80 |
| H(3B) | 9302(2) | 11261(4) | 3341(2) | 80 |
| H(5B) | 9129(3) | 8061(4) | 1937(3) | 80 |
| H(5A) | 8350(3) | 8698(4) | 2080(3) | 80 |
| H(8B) | 5372(2) | 5571(4) | 3310(3) | 80 |
| H(8A) | 5202(2) | 4665(4) | 2403(3) | 80 |
| H(9B) | 3609(2) | 6027(4) | 2513(3) | 80 |
| H(9A) | 4287(2) | 6449(4) | 3423(3) | 80 |
| H(11B) | 4205(2) | 3364(4) | 1898(2) | 80 |
| H(11A) | 3412(2) | 4044(4) | 1966(2) | 80 |

**Table 3.** Selected bond lengths (Å).

| | | | | | |
|---|---|---|---|---|---|
| V(1)–O(1) | 1.609(3) | V(1)–O(2) | 1.8085(7) | V(1)–O(6) | 1.982(3) |
| V(1)–O(3) | 1.976(3) | V(1)–O(8) | 2.043(3) | V(1)–N(1) | 2.283(3) |
| V(2)–O(16) | 1.611(3) | V(2)–O(15) | 1.8167(7) | V(2)–O(10) | 1.970(3) |
| V(2)–O(12) | 1.983(3) | V(2)–O(14) | 2.039(3) | V(2)–N(2) | 2.283(3) |

**Synthesis:** The synthetic method of the present complex is very different from that of complex $(NH_4)_3[V_2O_3(nta)_2]$ $3H_2O$ [8]. But they produced the similar crystal structure. It may indicate that the ligand of nta favors the formation of the crystal structure.

**Table 4.** Selected bond angles (°).

| | | | |
|---|---|---|---|
| O(1)–V(1)–N(1) | 168.60(14) | O(16)–V(2)–N(2) | 170.21(13) |
| O(1)–V(1)–O(2) | 104.18(12) | O(16)–V(2)–O(15) | 104.05(15) |
| O(1)–V(1)–O(3) | 104.68(14) | O(16)–V(2)–O(10) | 102.29(14) |
| O(1)–V(1)–O(6) | 102.14(14) | O(16)–V(2)–O(12) | 89.40(8) |
| O(1)–V(1)–O(8) | 91.58(14) | O(16)–V(2)–O(14) | 93.11(13) |
| O(2)–V(1)–O(6) | 90.13(9) | O(15)–V(2)–O(10) | 90.42(9) |
| O(2)–V(1)–O(3) | 89.99(9) | O(15)–V(2)–O(12) | 89.40(8) |
| O(2)–V(1)–O(8) | 164.24(9) | O(15)–V(2)–O(14) | 162.82(8) |
| O(2)–V(1)–N(1) | 87.00(8) | O(15)–V(2)–N(2) | 85.94(8) |
| O(3)–V(1)–N(1) | 77.14(11) | O(10)–V(2)–N(2) | 77.08(10) |
| O(3)–V(1)–O(8) | 86.26(12) | O(10)–V(2)–O(14) | 86.59(11) |
| O(3)–V(1)–O(6) | 152.29(11) | O(10)–V(2)–O(12) | 152.97(11) |
| N(1)–V(1)–O(8) | 77.25(11) | N(2)–V(2)–O(14) | 77.10(10) |
| N(1)–V(1)–O(6) | 75.19(10) | N(2)–V(2)–O(12) | 75.96(11) |
| O(6)–V(1)–O(8) | 86.17(13) | O(12)–V(2)–O(14) | 85.68(11) |

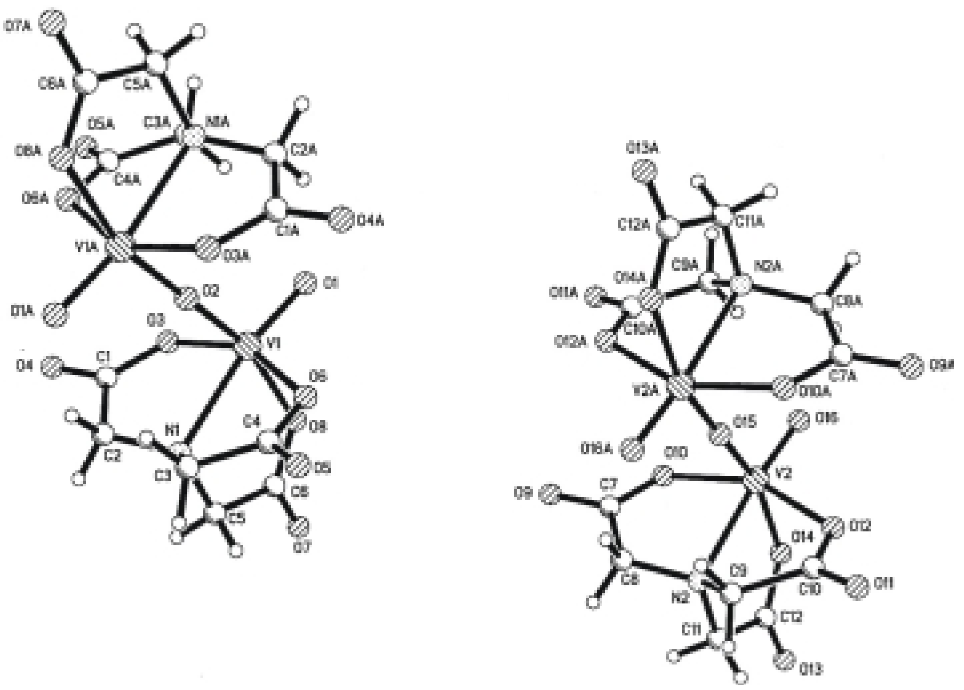

**Figure 1.** Crystal structure of the two binuclear groups of the complex.

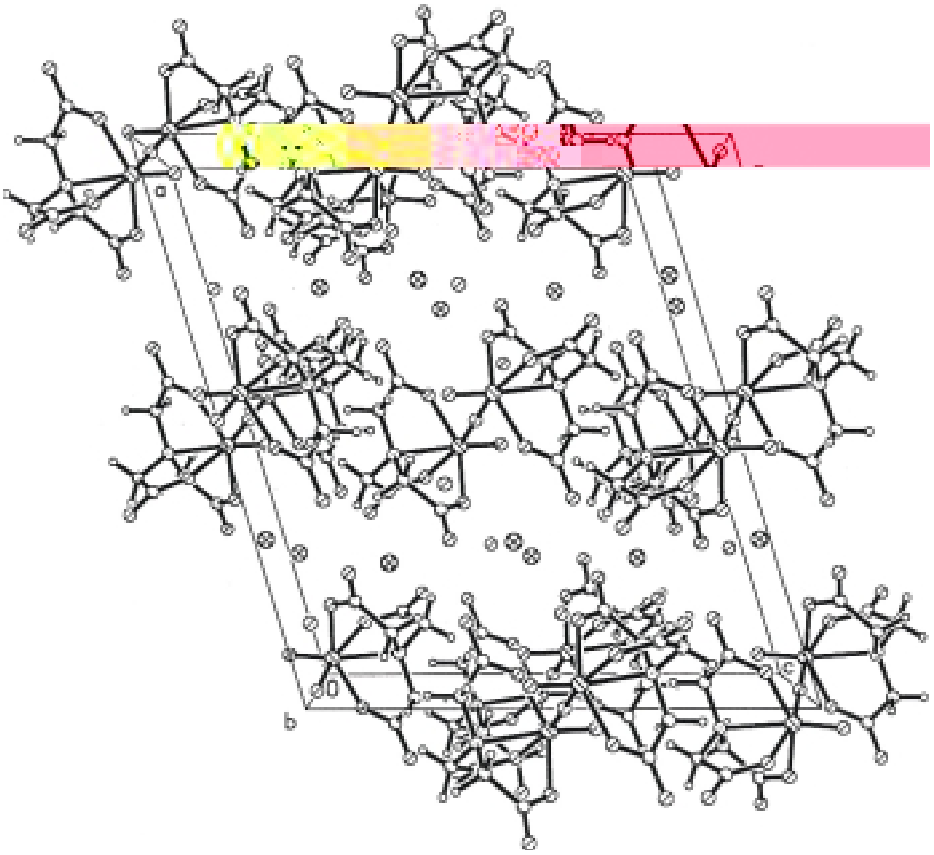

**Figure 2.** Cell packing diagram viewed along the b axis.

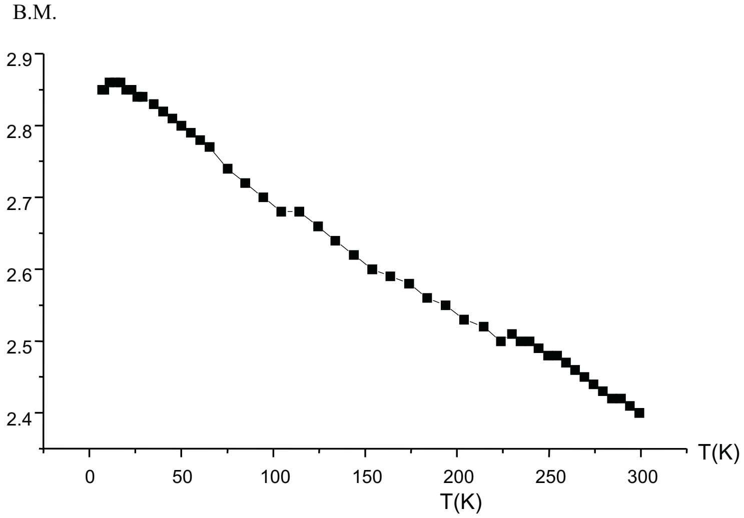

**Figure 3.** Relationship of the magnetic moments with temperature.

**Magnetic properties:** The magnetic moments of the two binuclear groups are shown in Figure 3. The magnetic moments increase as temperature falls, which indicates that there exists a weak ferromagnetic interaction between the two binuclear groups. The result is very different from that of similar structure complexes [13].

Acknowledgments

This paper was supported by the Nature Science Foundation of Shandong Province, the China Postdoctoral Science Foundation and the National Nature Science Foundation of China (No. 29671012 and 29733090).

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