Synthesis of Oxalato-Bridged (Oxo)vanadium(IV) Dimers Using L-Ascorbic Acid as Oxalate Precursor: Structure and Magnetism of Two Systems

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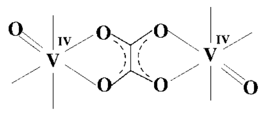
Keywords: Vanadium / Bridging ligands / Magnetic properties

The reaction of an aqueous solution of NH_4VO_3 with L-ascorbic acid and Et_4NBr has afforded $[Et_4N]_2[(VO)_2(C_2O_4)_3(H_2O)_2]\cdot 4H_2O$ (**3**). A similar reaction, in which malonic acid is also added, has furnished $[Et_4N]_2[(VO)_2(C_2O_4)(C_3H_2O_4)_2(H_2O)_2]\cdot 2H_2O$ (**4**). In these syntheses the oxalate ion is derived from L-ascorbic acid. In both the complexes the dinuclear anion is centrosymmetric. In **3** the metal atoms are displaced from the plane of the bridging oxalate anion by 0.05 Å, the corresponding displacement in **4** being 0.17 Å. The terminal oxalato chelate ring in **3** is roughly planar but the malonato chelate ring in **4** has a distorted boat conformation. The V−O distances in **4** are systematically shorter than the corresponding distances in **3** by 0.02−0.06 Å. The V···V distance within the dimer is 5.616(2) Å in **3** and 5.529(2) Å in **4**. The two uncoordinated water molecules in the asymmetric unit of **3** constitute a hydrogen-bonded dimer and the lattice consists of a supramolecular anionic assembly held by five different types of O···O hydrogen bonds. The anionic assembly in **4** involves three types of O···O hydrogen bonds. The Et_4N^+ cations reside between the anionic layers. The magnetic susceptibility data of both **3** and **4** fit excellently with the Heisenberg dimer model in the temperature interval 2−300 K. The species are antiferromagnetic and the J values are $-6.50\ cm^{-1}$ for **3** and $-6.25\ cm^{-1}$ for **4**. The two opposing factors — V−O(bridge) bond length and the displacement of the metal atom from the oxalate plane — appear to have more or less balanced each other resulting in virtually equal J values for the two complexes.

Introduction

There is a long-standing chemical interest in the interaction of metal ions with L-ascorbic acid.[1] Very few authentic metal ascorbates have, however, been isolated and characterized.[1−4] Our familiarity[5−8] with vanadate esters of polyols prompted us to scrutinize the use of L-ascorbic acid as a possible diol ligand towards vanadium. We have not succeeded in isolating vanadate esters of L-ascorbic acid but the study has furnished a new route for the synthesis of oxalato-bridged (oxo)vanadium dimers incorporating the moiety **1**. The structure and magnetism of two representative species are reported in the present work.



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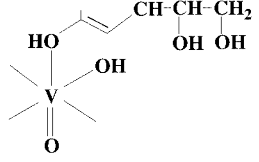
Results and Discussion

Synthesis

A rate study on the reaction of aqueous (oxo)vanadium(V) with L-ascorbic acid in strongly acidic media had suggested that a transient ascorbate complex is formed but it undergoes rapid redox transformation to (oxo)vanadium(IV) and dehydroascorbic acid.[9] In view of our diol work[5−8] the transient complex may have the bonding mode **2**.



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We have also failed to isolate a stable vanadium complex of L-ascorbic acid by the reaction of vanadium salts with L-ascorbic acid under different conditions of stoichiometry, pH and temperature. On the other hand, treatment of an aqueous solution of ammonium metavanadate with L-ascorbic acid and Et_4NBr in the ratio 1:1.5:1 at 70 °C gave a dark-green solution from which blue crystals of **3** slowly

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deposited in excellent yields. The mixed oxalato-malonato complex **4** was obtained by a similar procedure from ammonium metavanadate, L-ascorbic acid, malonic acid and Et_4NBr in the ratio 1:0.5:1:1.

$$[Et_4N]_2[(VO)_2(C_2O_4)_3(H_2O)_2]\cdot 4H_2O \tag{3}$$

$$[Et_4N]_2[(VO)_2(C_2O_4)(C_3H_2O_4)_2(H_2O)_2]\cdot 2H_2O \tag{4}$$

In the above syntheses, the oxalate ion is derived by oxidative/hydrolytic degradation [10−12] of L-ascorbic acid. As an in situ precursor of oxalic acid, L-ascorbic acid has recently found a use in the synthesis of oxalate complexes of metal ions;[13−15] we report here the first examples in the case of vanadium. Both **3** and **4** reported here are new compounds, although a few analogues of **3** synthesized from oxalic acid/oxalate are known.[16−18] Mononuclear oxalato chelates of (oxo)vanadium(IV) have been known for a long time.[19]

Characterization data are given in the Exp. Sect. The complexes display a V=O stretch near 980 cm^{-1} and multiple carboxylate vibrations in the region 800−1720 cm^{-1}. In aqueous solutions three ligand-field transitions occur in the visible region. Details are given in the Exp. Sect.

Structure

In both the complexes the dinuclear anion is centrosymmetric, the centre of inversion lying on the C−C bond of the bridging oxalato moiety. The asymmetric unit in each case corresponds to half the molecular formula. In **3** the Et_4N^+ cations lie in general positions while in **4** they lie on twofold axes passing through the nitrogen atoms. Views of the anions of **3** and **4** are shown in Figures 1 and 2, respectively. Selected bond parameters are listed in Table 1.

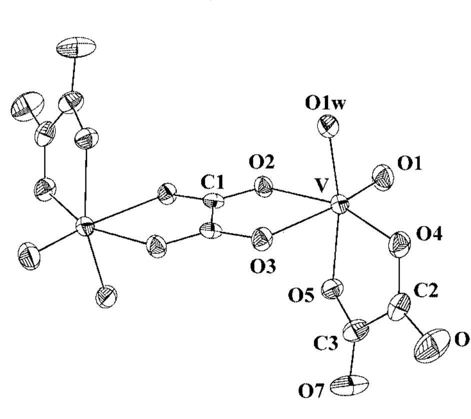


Figure 1. Perspective view and atom labeling scheme of $[(VO)_2(C_2O_4)_3(H_2O)_2]^{2-}$; all non-hydrogen atoms are represented by 30% thermal probability ellipsoids

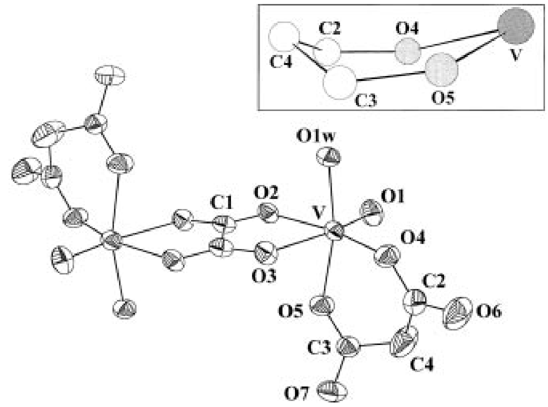


Figure 2. Perspective view and atom labeling scheme of $[(VO)_2(C_2O_4)(C_3H_2O_4)_2\ (H_2O)_2]^{2-}$; all non-hydrogen atoms are represented by 30% thermal probability ellipsoids

Table 1. Selected bond lengths [Å] and angles [°] for **3** and **4**

	3	**4**
Distances:		
V−O(1)	1.582(3)	1.561(6)
V−O(2)	2.023(3)	2.009(6)
V−O(3)	2.281(3)	2.218(6)
V−O(4)	1.993(3)	1.930(6)
V−O(5)	1.999(3)	1.953(6)
V−O(1w)	2.020(4)	2.013(7)
C(1)−O(2)	1.259(5)	1.248(10)
C(1A)−O(3)	1.235(5)	1.225(9)
C(2)−O(4)	1.295(6)	1.241(10)
C(3)−O(5)	1.263(6)	1.230(10)
C(2)−O(6)	1.214(6)	1.211(10)
C(3)−O(7)	1.210(6)	1.228(10)
Angles:		
O(1)−V−O(2)	97.2(2)	95.4(3)
O(1)−V−O(3)	172.8(2)	171.4(3)
O(1)−V−O(4)	103.7(2)	102.4(3)
O(1)−V−O(5)	102.6(2)	101.6(2)
O(1)−V−O(1w)	98.9(2)	98.2(3)
O(2)−V−O(3)	75.95(11)	76.1(2)
O(2)−V−O(4)	158.34(14)	162.1(3)
O(2)−V−O(5)	88.96(13)	88.1(2)
O(2)−V−O(1w)	90.5(2)	88.7(3)
O(3)−V−O(4)	83.37(13)	86.1(2)
O(3)−V−O(5)	79.63(12)	79.5(2)
O(3)−V−O(1w)	79.33(14)	80.8(3)
O(4)−V−O(5)	80.96(14)	89.1(3)
O(4)−V−O(1w)	92.0(2)	88.0(3)
O(5)−V−O(1w)	158.4(2)	160.2(3)

In **3** the $OV(C_2O_4)VO$ fragment defines a good plane of mean deviation 0.01 Å. In **4** the fragment is not quite planar (mean deviation 0.04 Å), the vanadium atoms being displaced by 0.17 Å above and below the nearly perfect plane of the oxalate anion (the corresponding displacement in **3** is only 0.05 Å). In **3** the terminal oxalato chelate rings are roughly planar (mean deviation 0.05 Å), the dihedral angle between them being 106.7°. In the $V(C_3H_2O_4)$ fragment of **4** the malonato chelate ring has a distorted boat shape (inset in Figure 2) in which the V and C4 atoms are displaced by 0.4 Å in the same direction from the plane of the O4, O5, C2, C3 atoms.

In the distorted octahedral VO_6 coordination spheres, the V−O(1) (oxo) and V−O(3) (*trans* to oxo) distances are shorter and longer, respectively, than the other distances in both **3** and **4**. The V−O distances in **4** are systematically shorter than the corresponding distances in **3** by 0.02−0.06

Å. The V···V distances within the dimer are 5.616(2) Å in **3** and 5.529(2) Å in **4**.

Hydrogen Bonding

The two uncoordinated water molecules (lattice water) in the asymmetric unit of **3** form a strongly hydrogen-bonded dimer, the O···O distance being 2.619(3) Å. The dimer is also involved in additional hydrogen bonding with coordinated and uncoordinated oxalato oxygen atoms and with the coordinated water molecule, which, in turn, is hydrogen-bonded to an uncoordinated oxalate oxygen atom. The lattice thus consists of a supramolecular anionic assembly held together by five different types of O···O hydrogen bonds (Table 2) as illustrated in Figure 3. The Et_4N^+ cations reside in between the anionic layers.

Table 2. Hydrogen bond lengths [Å] in **3** and **4**

3		**4**	
O4[a]···O2w[a]	2.822(5)	O6[c]···O2w	2.731(6)
O6···O2w	2.746(5)	O7[d]···O1w	2.591(5)
O7···O1w[b]	2.599(5)	O1w···O2w	2.678(5)
O1w[b]···O3w	2.701(5)		
O2w···O3w	2.619(5)		

[a] $1 - x, y, z$. [b] $1/2 - x, 1/2 + y, z$. [c] $-1/2 + x, 1 - y, 1/2 - z$. [d] $1/2 - x, y, 1/2 + z$.

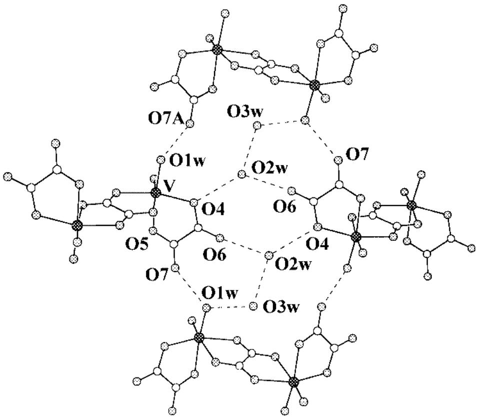


Figure 3. Hydrogen bonding in crystals of **3**

In the asymmetric unit of **4** there is only one lattice water, which is hydrogen-bonded to the coordinated water molecule and to an uncoordinated malonate oxygen atom. The coordinated water molecule is also hydrogen-bonded to an uncoordinated malonate oxygen atom. These three types of O···O hydrogen bonds generate the anionic assembly in the lattice of **4** (Figure 4, Table 2).

Magnetism

Magnetic data for **3** and **4** have been collected in the temperature range 2−300 K. Near perfect fits with the Heisenberg dimer model are attainable (Figures 5 and 6) using the parameters listed in Table 3. In both cases a susceptibility maximum occurs near 8 K and the compounds exhibit Curie−Weiss paramagnetism at high temperatures ($T >$ 50 K). The compounds are thus weakly antiferromagnetic and both the J values lie close to -6 cm^{-1}. The quality of

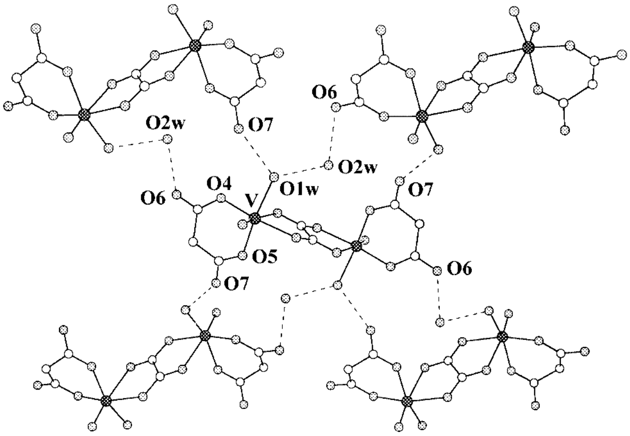


Figure 4. Hydrogen bonding in crystals of **4**

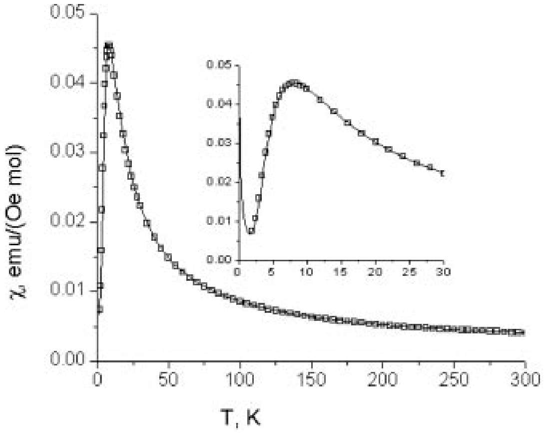


Figure 5. Variable-temperature magnetic susceptibility data of **3**; the solid line represents best fit to the dimer model

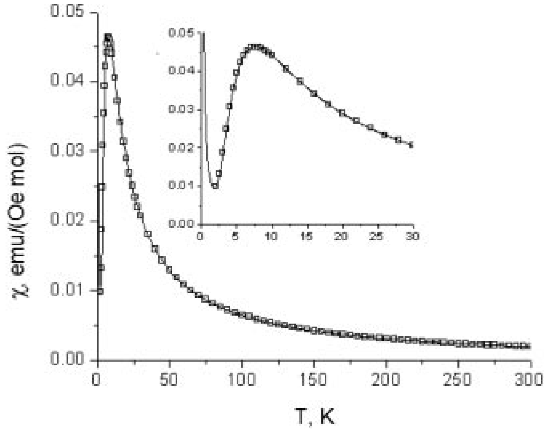


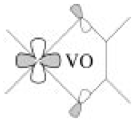
Figure 6. Variable-temperature magnetic susceptibility data of **4**; the solid line represents best fit to the dimer model

Table 3. Best-fit magnetic parameters

Compound	*g*	*J*	ρ	*tip*
3	1.93 ± 0.01	−6.50 ± 0.05	0.01 ± 0.002	0.0018 ± 0.00005
4	1.95 ± 0.01	−6.25 ± 0.05	0.02 ± 0.002	−0.0004 ± 0.00005

the fit to the dimer model indicates that, in spite of the extensive hydrogen bonding in the lattice, the interdimer magnetic interactions, if any, are small. Consistent[20] with the weak antiferromagnetism, polycrystalline samples of each compound display a virtually isotropic EPR signal at 77 K (**3**: $g = 1.969$; **4**: $g = 1.963$). No zero-field splitting or half-field signals are observed.

The (oxo)vanadium(IV) (d^1) magnetic orbital overlaps with the bridging oxygen orbitals only in the π-fashion as idealized in **5**. The resulting magnetic coupling in the dimer is expected to be relatively weak.[20] Compounds **3** and **4** provide a unique opportunity for qualitatively scrutinizing the effect of certain bond parameters (*a*, *b* and *h* as shown in **6**) on the strength of magnetic coupling.



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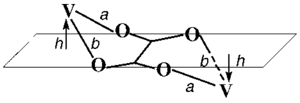
The shorter V−O (bridge) lengths (a = 2.009 Å, b = 2.218 Å) in **4** compared to those (a = 2.023 Å, b = 2.281 Å) in **3** may be expected to result in a stronger exchange coupling in **4**. On the other hand, the metal atom is much more displaced from the plane of the bridging oxalate in **4** (0.17 Å) than in **3** (0.05 Å) and this is expected to diminish the exchange interaction in **4**. The two opposing factors appear to have more or less balanced each other and the net bridge-mediated coupling of the magnetic orbitals in the two compounds are virtually equal.



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The present systems are somewhat stronger antiferromagnets than the two other structurally characterized compounds incorporating **1**: $[Ph_4P]_2[(VO)_2(C_2O_4)_3(H_2O)_2]\cdot 4H_2O$[17] ($J$ = −4.35 cm^{-1}) and $[(VO)_2(C_2O_4)(H_2O)_6]Cl_2\cdot Bu_4NCl\cdot H_2O$[21] ($J$ = −3.85 cm^{-1}). In $[(VO)_2(C_2O_4)(acac)_2(H_2O)_2]$[20] the value of J is −5.75 cm^{-1}, but its structure has not been determined.

Conclusion

Two oxalato-bridged (oxo)vanadium(IV) dimers **3** and **4** have been successfully assembled using L-ascorbic acid as an oxalate precursor. Structure determination has revealed significant differences in bond parameters of the $V(C_2O_4)V$ fragment in **3** and **4**. The V−O bond lengths follow the order **3** > **4** and the displacement of the metal atom from the bridging oxalate plane has the reverse order **4** > **3**. These inequalities act in opposite directions and the net antiferromagnetic coupling of the magnetic orbitals of the metal sites become virtually equal for **3** and **4** ($-J$ 6 cm^{-1}). Extensive hydrogen bonding is present in the lattice of both **3** and **4** but interdimer magnetic interactions are negligible.

Experimental Section

General: Ammonium metavanadate, L-ascorbic acid, malonic acid and tetraethylammonium bromide were obtained from S. D. Fine-Chem Ltd. All other chemicals and solvents were of analytical grade and were used as received. IR (KBr disk): Nicolet Magna IR 750 Series II spectrometer. UV/Vis: Shimadzu UVPC 1601 spectrometer. A Perkin−Elmer 2400 elemental analyzer was used for microanalysis (C,H,N).

$[Et_4N]_2[(VO)_2(C_2O_4)_3(H_2O)_2]\cdot 4H_2O$ (3): L-Ascorbic acid (0.113 g, 0.64 mmol) and tetraethylammonium bromide (0.09 g, 0.43 mmol) were added to a hot aqueous solution (20 mL) of NH_4VO_3 (0.05 g, 0.43 mmol). The solution was then stirred at 70 °C for 1 h. The dark-green solution thus obtained was further stirred at room temperature for 4 h and then left undisturbed exposed to air. After two weeks blue crystals were collected, washed with ethanol and air-dried. Yield: 0.28 g (84%). $C_{22}H_{52}N_2O_{20}V_2$ (766.5): calcd. C 34.47, H 6.84, N 3.66; found C 34.41, H 6.76, N 3.58. IR (KBr): $\tilde{\nu}$ = 984 (s, V=O), 1715, 1698 (s, C=O), 1658 (s, C=O), 1398, 1256 (s, C=O), 810 (m, O−C=O) cm^{-1}. UV/Vis (H_2O): λ_{max} (ε) = 595 sh (22), 783 (58), 960 sh nm (16 M^{-1}cm^{-1}).

$[Et_4N]_2[(VO)_2(C_2O_4)(C_3H_2O_4)_2(H_2O)_2]\cdot 2H_2O$ (4): L-Ascorbic acid (0.038 g, 0.22 mmol), malonic acid (0.045 g, 0.43 mmol) and tetraethylammonium bromide (0.09 g, 0.43 mmol) were added to a hot aqueous solution (20 mL) of NH_4VO_3 (0.05 g, 0.43 mmol). The blue solution thus obtained was treated as in the preparation of **3** furnishing blue crystals of **4**. Yield: 0.29 g (91%). $C_{24}H_{52}N_2O_{18}V_2$ (758.6): calcd. C 38.00, H 6.91, N 3.69; found C 37.91, H 6.96, N 3.56. IR (KBr): $\tilde{\nu}$: 975 (s, V=O), 1678, 1653 (s, C=O), 1589 (s, C=O), 1411, 1310 (s, C=O), 809 (m, O−C=O) cm^{-1}. UV/Vis (H_2O): λ_{max} (ε) =585 sh (19), 786 (65), 960 sh nm (13 M^{-1}cm^{-1}).

Crystal Structure Determination: Single crystals of complexes **3** and **4** were grown by slow evaporation of water from their aqueous solutions. Data were collected with a Nicolet R3m/V four-circle diffractometer with graphite-monochromated Mo-K_α radiation (λ = 0.71073Å) by the ω-scan technique in the range 3° ≤ 2θ ≤ 47° for **3** and 3° ≤ 2θ ≤ 50° for **4**. All data were corrected for Lorentz polarization, and an empirical absorption correction[22] was performed on each set of data on the basis of azimuthal scans

Table 4. Crystallographic data for **3** and **4**

	3	**4**
Empirical formula	$C_{22}H_{52}N_2O_{20}V_2$	$C_{24}H_{52}N_2O_{18}V_2$
M_r [g mol^{-1}]	766.54	758.56
Crystal size [mm]	0.40 × 0.30 × 0.20	0.48 × 0.38 × 0.36
T [K]	293(2)	293(2)
Crystal system	orthorhombic	orthorhombic
Space group	*Pbca* (no. 61)	*Pccn* (no. 56)
a [Å]	13.950(4)	14.382(6)
b [Å]	14.679(5)	16.295(9)
c [Å]	17.663(4)	14.220(10)
V [Å^3]	3617(2)	3332(3)
Z	4	4
Calcd. density [g cm^{-3}]	1.408	1.512
μ [mm^{-1}]	0.594	0.640
R_{int}	0.0187	0.0307
Refls. measured	2716	2955
Independent refls.	2684	2923
R_1 [$I > 2\sigma(I)$]	0.0517	0.0760
WR_2 [$I > 2\sigma(I)$]	0.1387	0.1830
Goodness of fit on F^2	1.055	1.011

of six reflections. All calculations of data reduction, structure solution, and refinement were done with the programs of SHELXTL, Version 5.03.[23] The two structures were solved by direct methods and were refined by full-matrix least squares on F^2. All non-hydrogen atoms were refined anisotropically. All the hydrogen atoms in both the structures were included in calculated positions. Significant crystal data are listed in Table 4. CCDC-200295 (**3**) and -200296 (**4**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge at www.ccdc.cam.ac.uk/conts/retrieving.html [or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; Fax: (internat.) + 44-1223/336-033; E-mail: deposit@ccdc.cam.ac.uk].

Magnetic Measurements: Magnetic data of polycrystalline samples (H = 1000 Oe) were recorded on 23.64 mg of **3** and 39.50 mg of **4** in the 2−300 K temperature range using a Quantum Design MPMS-5S SQUID Spectrometer. Calibration and operation procedures have been reported elsewhere.[24] The data were fitted to the Heisenberg dimer model of two S = 1/2 spins [Equation (1)] taking into account the presence of monomeric paramagnetic impurities (second term) and temperature-independent magnetism (third term), where χ is the magnetic susceptibility, T the temperature, g the g factor, J the exchange constant, *tip* is the temperature-independent contribution. The best-fit parameters are given in Table 3.

$$\chi = (1\text{-}\rho)\frac{N_A g^2 \mu_B^2}{k_B T}\,\frac{2\exp(\frac{2J}{k_B T})}{1+3\exp(\frac{2J}{k_B T})} + \rho\frac{N_A g^2 \mu_B^2}{2k_B T} + tip \quad (1)$$

The X-band EPR spectra of polycrystalline samples were measured with a Varian E-109C spectrometer fitted with a liquid nitrogen Dewar vessel using the following settings: sweep width 5000G, power 30dB, modulation 100 kHz, sweep center 3200 G, sweep time 240 s.

Acknowledgments

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