

Synthesis and Ferromagnetic Interaction in μ -Oxamido-Bridged Copper(II)–Oxovanadium(IV) Heterodinuclear Complexes

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Three new copper(II)–oxovanadium(IV) heterodinuclear complexes bridged by dianions of N,N'-oxamidobis(propionato)cuprate, [Cu(obp)] and end-capped with 1,10-phenanthroline (phen), 5-nitro-1,10-phenanthroline (NO₂-phen) or 5-chloro-1,10-phenanthroline (Cl-phen), have been synthesized and characterized; namely [Cu(obp)VO(phen)] (**1**), [Cu(obp)VO(NO₂-phen)] (**2**) and [Cu(obp)VO(Cl-phen)] (**3**). The three complexes have not yet been isolated in crystalline form suitable for X-ray structure analysis, but based on elemental analyses, IR and electronic spectra studies, magnetic moments at room-temperature and molar conductivity measurements, these complexes are proposed to have an extended oxamido-bridged structure consisting of planar copper(II) and square-pyramidal oxovanadium(IV) ions. The heterodinuclear complexes (**1**) and (**2**) were further characterized by variable-temperature magnetic susceptibility (4.2–300 K) measurements and the magnetic data have been also used to deduce the indicated heterodinuclear structure. The results derived from least-squares fit of the experimental data have confirmed that the operation of a ferromagnetic interaction between the adjacent oxovanadium(IV) and copper(II) ions through the oxamido-bridge within each molecule. Based on spin Hamiltonian, $\hat{H} = -2J\hat{S}_1 \cdot \hat{S}_2$, the exchange integral (J) was evaluated as $J = +11.68 \text{ cm}^{-1}$ for (**1**) and $J = +10.27 \text{ cm}^{-1}$ for (**2**). The influence of the symmetry of the magnetic orbitals on the nature of the magnetic interaction between the paramagnetic centers is also discussed.

Key words: oxamido-bridge, Cu(II)–VO(IV), heterodinuclear complexes, ferromagnetic interaction

The syntheses and magnetic investigations of ferromagnetic polynuclear metal complexes are of current interest [1–4], not only for gaining some insights into the electronic and geometric structure of metalloproteins and enzymes and thus correlating structure with biological function, but also for understanding fundamental factors governing the magnetic properties of transition-metal complexes and to find appropriate systems applicable as building units for the design of molecular-based ferromagnets. So far, much effort has been devoted to the design of high-spin molecules and several strategies have been proposed along this line [5–8]. Kahn has pointed out that accidental orthogonality and strict orthogonality of magnetic orbitals may give

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rise to a ferromagnetic spin coupling between neighbouring paramagnetic metal ions [6]. The former depends on some structural factors in a subtle manner. It appears that the accidental orthogonality of magnetic orbitals is hardly applied for the design of ferromagnetic complexes because of difficulties in finding the optimum structural conditions for it to occur and, in particular, in materializing such steric conditions in designed metal complexes. The strict orthogonality of magnetic orbitals, on the other hand, can be attained by choosing an appropriate combination of paramagnetic metal ions, and hence the design of ferromagnetic complexes based on this principle seems promising [5,8]. It is known that a combination of oxovanadium(IV) and copper(II) ions can give rise to such a strict orthogonality of magnetic orbitals [9,10]. The feasibility of this strategy has been revealed by magnetic analyses of some of copper(II)–oxovanadium(IV) heterodinuclear complexes [9,10]. However, as far as we are aware, examples of such heteronuclear complexes are still few, and to the best of our knowledge no heterodinuclear copper(II)–oxovanadium(IV) complex bridged by an oxamido group has so far been reported, although the oxamide bridge has been shown to be an excellent multiatom bridge for studying magnetic properties and many polynuclear complexes with bridging oxamide groups have been synthesized and magnetically characterized [7,11–13]. Taking into account the above facts, it is of considerable interest to synthesize and study Cu(II)–VO(IV) dinuclear complexes with bridging oxamide groups in order to gain some insight into the molecular magnetism of this kind of complexes.

In this paper, three new heterodinuclear Cu(II)–VO(IV) complexes described by the overall formula [Cu(obp)VO(L)] (L = phen, NO₂-phen, Cl-phen) have been synthesized and characterized by using sodium N,N'-oxamidobis(propionato)cuprate(II), Na₂[Cu(obp)]·3.5H₂O, as bridging ligand and the cryomagnetic properties of the [Cu(obp)VO(phen)] (**1**) and [Cu(obp)VO(NO₂-phen)] (**2**) complexes have been measured in the temperature range 4.2–300 K to examine the effect of the oxamido bridge upon the magnetic interaction between copper(II) and oxovanadium(IV) ions. The main result of this investigation is that the copper(II) and oxovanadium(IV) ions are coupled in a ferromagnetic fashion through the oxamido bridge. At present, the three dinuclear complexes have not been obtained in crystalline form suitable for X-ray structure analysis. However, the combination of magnetic studies and spectral data clearly demonstrates the presence of exchange coupling between the metal ions, reveals certain electronic properties of the heterodinuclear complexes, and allows predictions of structural features to be made.

EXPERIMENTAL

Materials: All of the reagents used in the synthesis were of analytical grade. VOSO₄·3H₂O and the terminal ligands 1,10-phenanthroline (phen); 5-nitro-1,10-phenanthroline (NO₂-phen) and 5-chloro-1,10-phenanthroline (Cl-phen) were used as commercially obtained. The mononuclear complex Na₂[Cu(obp)]·3.5H₂O was synthesized as previously described [13].

Synthesis of [Cu(obp)VO(phen)] (1): To a solution of $\text{Na}_2[\text{Cu}(\text{obp})] \cdot 3.5\text{H}_2\text{O}$ (0.369 g, 1 mmol) stirred in methanol (10 mL) was added successively a solution of $\text{VOSO}_4 \cdot 3\text{H}_2\text{O}$ (0.440 g, 1.1 mmol) in methanol (20 mL). The stirring was continued at room temperature (about 30 minutes) until the mixture became limpid. It was then filtered to eliminate impurities. To the resulting clear solution was added a methanol solution (15 mL) of phen (0.182 g, 1 mmol). The color of the solution turned from violet to dark-brown immediately, and the mixture was subsequently refluxed for *ca.* 12 h. After cooling to room temperature, dark-brown microcrystals thus formed were collected by suction filtration, washed several times with methanol, water and diethyl ether and dried over P_2O_5 under reduced pressure. Recrystallization was carried out from a DMF/ethanol (1:2) mixture. Yield: 0.404 g (75%), m.p. 229.5°C. Anal. calc. for $(\text{VO})\text{CuC}_{20}\text{H}_{16}\text{N}_4\text{O}_6$ (M.W. 538.86): C, 44.58; H, 2.99; N, 10.40; Cu, 11.79; VO, 12.42%. Found: C, 44.41; H, 3.10; N, 10.12; Cu, 11.57; VO, 12.25%.

Synthesis of [Cu(obp)VO(NO₂-phen)] (2): This complex was obtained as brown microcrystals by the same procedure and the same amount of reagents as above but using NO₂-phen (0.225 g, 1 mmol) instead of phen. It was recrystallized from a hot acetonitrile solution. Yield: 0.479 g (82%), m.p. 207.1°C. Anal. calc. for $(\text{VO})\text{CuC}_{20}\text{H}_{15}\text{N}_5\text{O}_8$ (M.W. 583.85): C, 41.14; H, 2.59; N, 12.00; Cu, 10.88; VO, 11.47%. Found: C, 41.36; H, 2.45; N, 11.78; Cu, 10.65; VO, 11.24%.

Synthesis of [Cu(obp)VO(Cl-phen)] (3): This complex was obtained as a pale-red powder by the same procedure and the same amounts of reagents as complex (1) but using Cl-phen (0.215 g, 1 mmol) instead of phen. Yield: 0.447 g (78%); m.p. 187.6°C. Anal. calc. for $(\text{VO})\text{CuC}_{20}\text{H}_{15}\text{N}_4\text{O}_6\text{Cl}$ (M.W. 573.30): C, 41.90; H, 2.64; N, 9.77; Cu, 11.08; VO, 11.68%. Found: C, 41.74; H, 2.79; N, 9.52; Cu, 10.86; VO, 11.41%.

Physical measurements: Carbon, hydrogen and nitrogen elemental analyses were performed with a Perkin-Elmer elemental analyzer Model 240. The metal contents were determined on an ICP-4300 inductively coupled plasma emission spectrophotometer. IR spectra were recorded with a NICOLET FT-IR 5DX spectrophotometer using KBr pellets. The electronic spectra (in acetonitrile solutions) were measured on a Cary 300 spectrophotometer. Molar conductances were measured with a Shanghai DDS-11A conductometer. Magnetic susceptibility measurements at room temperature were carried out by Gouy's method using $\text{Hg}[\text{Co}(\text{SCN})_4]$ as the calibrant. Variable temperature magnetic susceptibilities (4.2–300 K) were measured using a Quantum Design MPMS SQUID magnetometer. Diamagnetic corrections were made with Pascal's constants [14] for all the constituent atoms and effective magnetic moments were calculated by the equation $\mu_{\text{eff}} = 2.828(\chi_{\text{M}}T)^{1/2}$, where χ_{M} is the molar magnetic susceptibility corrected for diamagnetisms of the constituting atoms.

RESULTS AND DISCUSSION

Synthetic route and coordination environment of the dinuclear complexes: A promising method to design and synthesize heterodinuclear complexes is to use "complex ligand" that contains a potential donor group capable of coordinating to another metal ion [7–11]. In this study, our purpose was to obtain Cu(II)–VO(IV) heterodinuclear complexes, therefore, this synthetic method was adopted. As "ligand complex" we have chosen sodium N,N'-oxamidobis(propionato)cuprate(II), $\text{Na}_2[\text{Cu}(\text{obp})] \cdot 3.5\text{H}_2\text{O}$, which was first used to prepare alternating Cu(II)–Mn(II) bimetallic chain compound $\text{MnCu}(\text{obp})(\text{H}_2\text{O})_3 \cdot \text{H}_2\text{O}$ by Kahn *et al.* [13], as a bidentate mononuclear fragment, because it can coordinate to another metal ion through the oxamido oxygens to afford polynuclear species, and the remarkable efficiency of the oxamidate bridge to transmit electronic effects between the metal ions. Simultaneously, 1,10-phenanthroline (phen), 5-nitro-1,10-phenanthroline (NO₂-phen) and 5-chloro-1,10-phenanthroline (Cl-phen), respectively, were used as terminal ligands. Indeed, elemental analyses indicate that the reaction of $\text{Na}_2[\text{Cu}(\text{obp})] \cdot 3.5\text{H}_2\text{O}$ with $\text{VOSO}_4 \cdot 3\text{H}_2\text{O}$

and L (L = phen, NO₂-phen, Cl-phen) in *ca.* 1:1:1 mole ratio yielded the heterodinuclear complexes of the general formula [Cu(obp)VO(L)], as expected. These complexes are the first examples of Cu(II)–VO(IV) heterodinuclear complexes bridged by N,N'-oxamidobis(propionato)cuprate(II). Although crystal structures of the three heterodinuclear complexes are not known, the magnetic and spectroscopic data are sufficient to deduce the occurrence of a magnetically coupled heterodinuclear unit containing one copper(II) and one oxovanadium(IV) ions. On the basis of the physical and chemical evidence, the three heterodinuclear complexes may be presumed to have the coordination environment as shown in Figure 1.

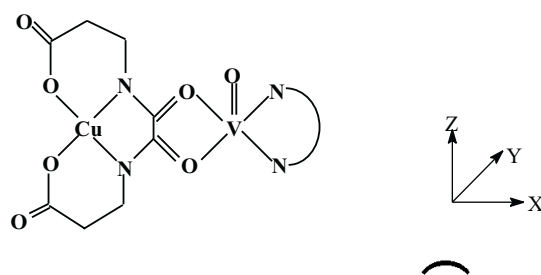


Figure 1. Plausible coordination environments of the complexes (N N = phen, NO₂-phen, Cl-phen).

Molar conductances and general properties of the dinuclear complexes: All of the Cu(II)–VO(IV) dinuclear complexes are sparingly soluble in water, methanol, ethanol, carbon tetrachloride, chloroform and benzene; but are soluble in acetonitrile, DMF and DMSO to give stable solutions at room temperature. In the solid state all of the dinuclear complexes are fairly stable in air so as to facilitate physical measurements. For the three Cu(II)–VO(IV) dinuclear complexes, the molar conductance values (1×10^{-3} mol·L⁻¹ acetonitrile solutions) fall in the expected range for non-electrolytes [15] (see Table 1). This is consistent with the elemental analyses data and the presumed structure of the complexes shown in Figure 1. The structure of the dinuclear complexes was further supported by the spectroscopic characterization and magnetic studies.

Infrared spectra: The IR spectra taken in the region 4000~400 cm⁻¹ provide some information regarding the mode of coordination in the dinuclear complexes and were analyzed in a careful comparison with that of the mononuclear fragment Na₂[Cu(obp)]·3.5H₂O. Since the IR spectra of the three dinuclear complexes are similar, the discussion is confined to the most important vibrations of 400~4000 cm⁻¹ region to the structure. The most relevant IR absorption bands from the IR spectra of the complexes along with their assignments are shown in Table 1. We will only discuss here selected infrared bands. It is noteworthy that the IR spectrum of the carbonyl stretching vibration at 1610 cm⁻¹ for Na₂[Cu(obp)]·3.5H₂O is considerably shifted towards higher frequencies (*ca.* 40~50 cm⁻¹) in the dinuclear complexes. This might be due to the following reasons. In general, when the deprotonated amide nitrogen is coordinated to the metal ion, its amide I band shifts considerably towards lower

wave numbers. In the case of an oxamide dianion coordinated to two metal ions as bridging ligands, the amide I band reverts to near its original position (in the protonated species) [12]. Although the amide I is due to a composite N–C=O vibration, it can essentially be seen as $\nu(\text{C}=\text{O})$. It is likely that the bond order of C=O (carbonyl) in the dinuclear complexes is higher than that in the corresponding mononuclear complex $\text{Na}_2[\text{Cu}(\text{obp})] \cdot 3.5\text{H}_2\text{O}$. This shift has often been used as a diagnostic indicator for oxamido-bridged structures [12]. Thus, the above observations mean that the carbonyl oxygen atoms of the complex ligand are coordinated with oxovanadium(IV) ion and are indicative of the oxamido-bridged structures. The facts that the carbonyl (C=O) deformation at 728 cm^{-1} of the ligand complex, $\text{Na}_2[\text{Cu}(\text{obp})] \cdot 3.5\text{H}_2\text{O}$, disappeared in the spectra of the dinuclear complexes, and accompanied by the appearance of a new band at *ca.* 520 cm^{-1} due to $\nu(\text{V}-\text{O})$ further confirm the coordinated nature of the carbonyl oxygens in these heterodinuclear complexes [11, 13]. The coordination mode of the oxamido group has been supported by the crystal structure of an analogous complex [13]. On the other hand, the antisymmetric stretching vibration of the carboxylate group for $\text{Na}_2[\text{Cu}(\text{obp})] \cdot 3.5\text{H}_2\text{O}$ remains at 1575 cm^{-1} in the dinuclear complexes, indicating that the carboxylate groups in the mononuclear complex are not coordinated with the oxovanadium(IV) ion. Furthermore, the –N=C– stretching vibrations for the terminal ligands (phen, NO_2 -phen, Cl-phen) were found in the corresponding dinuclear complexes (see Table 1), suggesting that the N atoms of the terminal ligands are coordinated with the oxovanadium(IV) ion. The additional band observed at around 430 cm^{-1} due to $\nu(\text{V}-\text{N})$ further supports this view. In addition, the V=O stretching vibrations of all heterodinuclear complexes were observed near 990 cm^{-1} , indicating no intermolecular $\text{V}=\text{O} \cdots \text{V}=\text{O}$ bonding in these complexes [16]. This is consistent with the following magnetic analysis (*vide infra*). Besides these observations, a broad intense band centered at *ca.* 1120 cm^{-1} , typical for a non-coordinated sulfate anion [17] was not observed for all dinuclear complexes, which coincides with the conductance data of the heterodinuclear complexes.

Table 1. Physical data.

Complexes	$\Lambda_{\text{M}}^{\text{a}}$	IR (cm^{-1})						μ_{eff} (B.M.)
		$\nu(\text{CO}_2^-)$	$\nu(\text{C}=\text{O})$	$\nu(\text{N}=\text{C})$	$\nu(\text{V}-\text{O})$	$\nu(\text{V}-\text{N})$	$\nu(\text{V}=\text{O})$	
$\text{Na}_2[\text{Cu}(\text{obp})] \cdot 3.5\text{H}_2\text{O}$		1575	1610					
$[\text{Cu}(\text{obp})\text{VO}(\text{phen})]$	8	1575	1652	1530	520	430	995	2.62
$[\text{Cu}(\text{obp})\text{VO}(\text{NO}_2\text{-phen})]$	5	1575	1665	1528	521	432	996	2.59
$[\text{Cu}(\text{obp})\text{VO}(\text{Cl-phen})]$	12	1575	1650	1525	526	435	992	2.65

^aValues for $1 \times 10^{-3}\text{ mol} \cdot \text{L}^{-1}$ acetonitrile solution, unit: $\text{S} \cdot \text{cm}^2 \cdot \text{mol}^{-1}$.

Table 2. Electronic spectra.

Complexes	UV (cm ⁻¹)/ ϵ_{\max} (mol ⁻¹ ·cm ⁻¹ ·L)				
	CT	² B _{1g} → ² E _g	d _{xy} → d _{xz, yz}	d _{xy} → d _{x²-y²}	d _{xy} → d _{z²}
[Cu(obp)VO(phen)]	31500(28800)	18320(220)	14100(40)	17800(50)	24400(58)
[Cu(obp)VO(NO ₂ -phen)]	32800(26500)	18380(235)	13600(36)	18000(55)	24200(70)
[Cu(obp)VO(Cl-phen)]	32300(23600)	18350(198)	13900(30)	17950(62)	24900(45)

Electronic spectra: In order to obtain further structural information, the electronic spectra of the mononuclear fragment Na₂[Cu(obp)]·3.5H₂O and the Cu(II)–VO(IV) heterodinuclear complexes were measured in acetonitrile solutions, and the assignments were made on the basis of a careful comparison of the latter with the former. The electronic absorption spectral data for these complexes are given in Table 2. As shown in this Table, the electronic spectra of the three heterodinuclear complexes are similar to each other. For all three dinuclear complexes, three weak absorption peaks may be assigned to d-d transitions of the oxovanadium(IV) ion in a five-coordinate, square-pyramidal environment (C_{4v}) [18], while a strong band at *ca.* 18.3×10³ cm⁻¹ may be attributed to the ²B_{1g} → ²E_g transition of the “inside” copper(II) in a square-planar environment [18]. The frequency is higher than that for the mononuclear copper(II) complex Na₂[Cu(obp)]·3.5H₂O (16.8×10³ cm⁻¹). Such a blue-shift of copper(II) ion in the d-d band may be attributed to the increased ligand field strength for [CuN₂O₂] chromophore on forming a dinuclear complex with an oxovanadium(IV) ion [19]. In addition, a stronger absorption in the short wavelength range (see Table 1) may be attributable to the charge-transfer absorption bands, which may be due to the spin-exchange interaction between the copper(II) and oxovanadium(IV) ions through the π -path orbital set up by an oxamido bridge [12]. Further investigations of these and similar systems are required in order to obtain more detailed assignment for charge transfer.

All our efforts to grow crystals of these copper(II)–oxovanadium(IV) dinuclear complexes suitable for X-ray structure determination so far have been unsuccessful. However, based on the composition of these dinuclear complexes, their IR and electronic spectra, conductivity measurements, magnetic studies (*vide infra*), these complexes are proposed to have an extended oxamido-bridged structure and to contain a copper(II) ion and an oxovanadium(IV) ion, which have a square-planar environment and a square-pyramidal environment, respectively, as shown in Figure 1. The plausible structure is further illustrated by the following magnetic studies.

Magnetic studies: The observed magnetic moment per dinuclear complex at room temperature, shown in Table 1, is slightly higher than the spin-only value (2.45 B.M.) for the magnetically non-interacting of Cu(II)–VO(IV) (S_{Cu} = 1/2, S_{VO} = 1/2) heterodinuclear complexes. This suggests the operation of ferromagnetic spin-exchange interaction in these complexes [11,20]. In order to obtain further information on the structure of the complexes, the magnetic data have been used to deduce the indicated dinuclear structure. Thus, variable-temperature molar susceptibility (4.2~300 K) data were collected for complexes [Cu(obp)VO(phen)] (**1**) and

[Cu(obp)VO(NO₂-phen)] (**2**), by way of example, and the results are shown in Figure 2 in the form of plots of χ_M vs. T and μ_{eff} vs. T, where χ_M , μ_{eff} and T denote molar susceptibility, effective magnetic moment and absolute temperature, respectively. From Figure 2 it is evident that the magnetic behavior of the two dinuclear complexes is similar. As the temperature is lowered, the effective magnetic moments increase gradually. This is typical of a ferromagnetic coupling between copper(II) and oxovanadium(IV) ions through the oxamido-bridge within each dinuclear unit [11] and implies the existence with the room-temperature magnetic moments of the dinuclear complexes.

In order to understand quantitatively the nature and magnitude of the spin-exchange interaction, the magnetic analysis was carried out using the Bleaney-Bowers susceptibility equation [21] based on the Heisenberg operator ($\hat{H} = -2J\hat{S}_1 \cdot \hat{S}_2$, $S_1 = S_2 = 1/2$):

$$\chi_M = \frac{2N\beta^2 g^2}{kT} [3 + \exp(-2J/kT)]^{-1} + N\alpha \quad (1)$$

where χ_M denotes the molecular susceptibility per dinuclear complex, $N\alpha$ is the temperature-independent paramagnetism ($120 \times 10^{-6} \text{ cm}^3 \cdot \text{mol}^{-1}$) and the remaining symbols have their usual meanings. As shown in Figure 2, good least-squares fits to the experimental data were obtained with equation (1) for complexes (**1**) and (**2**). The determined magnetic parameters and the agreement factor F, defined here as $F = \Sigma[(\chi_M)_{\text{calc}} - (\chi_M)_{\text{obs}}]^2 / \Sigma(\chi_M)_{\text{obs}}$ are: $J = +11.68 \text{ cm}^{-1}$, $g = 2.09$, $F = 3.9 \times 10^{-4}$ for (**1**) and $J = +10.27 \text{ cm}^{-1}$, $g = 2.06$, $F = 5.5 \times 10^{-4}$ for (**2**). These results have confirmed that the spin coupling between oxovanadium(IV) and copper(II) ions through an oxamido-bridge within each dinuclear molecule is ferromagnetic. The ferromagnetic spin-exchange interaction between oxovanadium(IV) and copper(II) ions within each dinuclear unit may be explained by several models which have so far been proposed [22–24]. According to these models, strict orbital orthogonality results in ferromagnetism ($J > 0$), otherwise an antiferromagnetic coupling ($J < 0$) should be involved in the system. For the present dinuclear complexes, if the coordinates used are shown by Figure 1, in a 4+1 environment, the most destabilized orbital occupied by the unpaired electron of copper(II) ion is of the d_{xy} -type. The unpaired electron of oxovanadium(IV) ion (configuration d^1) occupies a $d_{x^2-y^2}$ type orbital. Thus, the magnetic orbital Φ_{Cu} in copper(II)–oxovanadium(IV) heterodinuclear complexes is asymmetric with regard to a mirror plane containing the metals and perpendicular to the dinuclear molecule unit, while the magnetic orbital Φ_{VO} is symmetric with regard to the mirror-plane. Consequently, the overlap integral $\langle \Phi_{\text{Cu}} | \Phi_{\text{VO}} \rangle$ in the present copper(II)–oxovanadium(IV) dinuclear complexes is equal to zero. This may be the reason for a ferromagnetic spin-exchange interaction observed in the these copper(II)–oxovanadium(IV) heterodinuclear complexes.

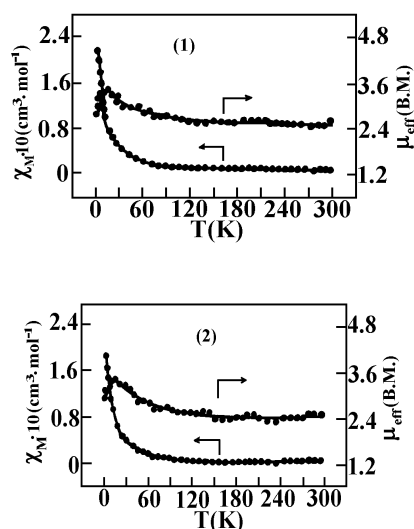


Figure 2. Temperature variation of χ_M (lower curve) and μ_{eff} (upper curve) for the complexes [Cu(obp)VO(phen)] (1) and [Cu(obp)VO(NO₂-phen)] (2). The curves are based on equation (1) using the parameters given in the text. (●), experimental data; (—), calculation curves as described in the text.

It is clear from the above discussion that the strict orthogonality of magnetic orbitals can be attained by choosing an appropriate combination of paramagnetic metal ions, and hence the design of ferromagnetic complexes based on this principle opens vast perspectives [6,9]. Indeed, further investigations on this and similar systems are still required in order to get a deeper insight into this exciting field of magnetic interactions and are in progress in our laboratory.

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