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Dinuclear (Cu/Cu, Ni/Ni, V/V and Fe/Fe) complexes of a novel oxamide-type ligand coordinating in the *trans* conformation

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Abstract

The preparation and characterization of an original N,N'-disubstituted oxamide derivative are reported. This compound is distinguished by the occurrence of substituents with terminal NH_2 groups which can be used in further reactions. Thus by reaction with salicylaldehyde one obtains a new dinucleating ligand which affords the first examples of vanadium(IV) and iron(III) oxamido-bridged dinuclear complexes. The spectroscopic characteristics and magnetic properties of these complexes and the related nickel(II) and copper(II) complexes are reported.

Introduction

Polymetallic systems are attractive as synthetic models of the active sites of metallobiomolecules and also as materials for studying correlations between structure and cooperative physical properties. Quite recently, the possibility of using suitable polynuclear complexes as starting materials for the synthesis of metallic oxides has been documented [1].

Among the known polynucleating ligands, oxamide derivatives are receiving considerable attention due to their possibilities. First, the oxamide bridge is known to be very efficient in transmitting exchange interaction between magnetic ions in favourable geometries [2–17]. Further, these ligands are easily altered to yield new derivatives designed for particular problems. Like the oxalate dianion, the oxamide dianion can act as a chelating or a bis-chelating ligand for the first row transition metal ions but the development of its coordination chemistry is hindered by its low solubility in common solvents and its sensitivity to hydrolytic decomposition [5, 18–22]. To overcome these drawbacks, use is made of N-substituted or N,N'-disubstituted derivatives which contain a donor group X within the substituent(s) (Fig. 1). Indeed, if this condition is not fulfilled, complexation does not occur. Very often X is an amino group. In this instance a disubstituted dioxamide coordinating in the *cis* conformation displays two different sites: an inner site N_2N_2 which is generally occupied by a copper(II) or nickel(II) ion and an outer site O_2 which can accommodate a large variety of metal ions [2, 12, 14, 16, 17, 23]. When the ligand adopts the *trans* conformation the two sites become identical N_2OY [2–4, 7, 24, 25] (Y representing an exogeneous donor) and, in most of the reported complexes they are occupied by copper(II) ions. This probably originates in the fact that the ligands are seldom isolated. Their synthesis is run in the presence of copper ions (template synthesis) so that the final products are merely the related copper complexes. Recently some ligands have been isolated [15, 16, 26] but the donor groups X they contain are secondary (–NHR) or tertiary (–NRR') amino residues but not primary ($-NH_2$) groups. Owing to the intrinsic reactivity of the later residue which would allow further structural modification to be performed, we have prepared the precursor H_2L^1 and, via reaction of its terminal $-NH_2$ group, the new binucleating ligand H_4L^2 (Fig. 2). As expected, H_4L^2 displays a good solubility in common solvents. Its coordination chemistry is not restricted to Cu(II) and Ni(II) as are H_4L^3 and other related ligands. Indeed, we succeeded in preparing the first examples of vanadium(IV) and iron(III) ox-

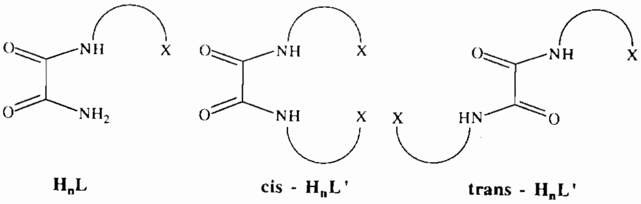

Fig. 1. Chelating (H_nL) and bis-chelating (H_nL') oxamide ligands.

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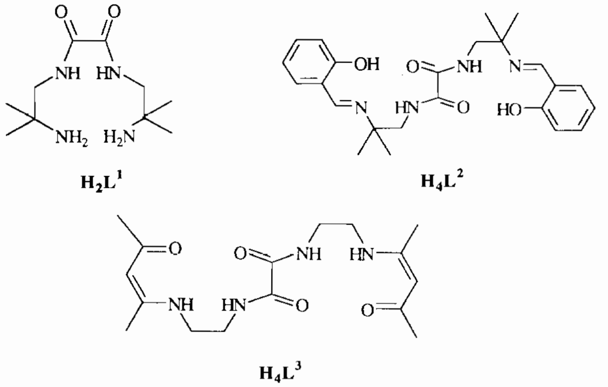

Fig. 2. Precursor (H_2L^1), new binucleating ligand (H_4L^2) and reference ligand (H_4L^3).

amidato-bridged dinuclear complexes, $VO(L^2)VO$ and $ClFe(L^2)FeCl$.

Experimental

Ligand H_2L^1

To 1,2-diamino-2-methylpropane (5 g; 5.7×10^{-2} M) in diethyl ether (60 ml), was added ethyl oxalate (4.2 g; 2.8×10^{-2} M) at one go. Three hours later, the white precipitate was filtered, washed with ether, and dried. Yield 90%. *Anal.* Calc. for $C_{10}H_{22}N_4O_2$: C, 52.2; H, 9.6; N, 24.3. Found: C, 52.1; H, 9.8; N, 24.0%.

Ligand H_4L^2

To the aforementioned ligand H_2L^1 (3 g; 1.3×10^{-2} M) in methanol (50 ml) was added salicylaldehyde (3.2 g; 2.6×10^{-2} M). The solution was stirred and heated at reflux for 15 min and allowed to cool, leaving a yellow precipitate which was filtered, washed with methanol, ether and dried. Yield 95%. *Anal.* Calc. for $C_{24}H_{30}N_4O_4$: C, 65.8; H, 6.9; N, 12.8. Found: C, 65.7; H, 7.1; N, 12.7%.

Complexes

$Cu(L^2)Cu$

To a methanolic solution (30 ml) of H_4L^2 (0.3 g; 6.8×10^{-4} M) was added a methanolic solution of $CuAc_2\cdot H_2O$ (0.27 g; 1.4×10^{-3} M). Stirring and heating the mixture to reflux for 20 min induced the appearance of a violet precipitate. Filtering of the cooled solution yielded the desired product which was washed with methanol and ether. Yield 85%. *Anal.* Calc. for $C_{24}H_{26}Cu_2N_4O_4$: C, 51.3; H, 4.6; N, 10.0. Found: C, 51.0; H, 4.7; N, 9.9%.

$Ni(L^2)Ni$

The same experimental procedure starting with $NiAc_2\cdot 4H_2O$ yielded a red precipitate in an 80% yield. *Anal.* Calc. for $C_{24}H_{26}N_4Ni_2O_4$: C, 52.2; H, 4.7; N, 10.1. Found: C, 51.9; H, 4.8; N, 9.9%.

$VO(L^2)VO$

To a methanolic solution (40 ml) of H_4L^2 (0.3 g; 6.8×10^{-4} M) was added $VOSO_4$ (0.22 g; 1.4×10^{-3} M) and NEt_3 (0.38 ml; 2.7×10^{-3} M). After heating and stirring, the green precipitate was filtered from the cooled solution, washed with water, then methanol and ether. Yield 75%. *Anal.* Calc. for $C_{24}H_{26}N_4O_6V_2$: C, 50.7; H, 4.6; N, 9.9. Found: C, 51.0; H, 4.7; N, 10.0%.

$ClFe(L^2)FeCl$

To a methanolic solution (30 ml) of H_4L^2 (0.5 g; 1.1×10^{-3} M) were added $FeCl_3$ (0.38 g; 2.3×10^{-3} M) in MeOH (15 ml) and then NEt_3 (0.65 ml; 4.6×10^{-3} M). The mixture was stirred and heated to reflux for 30 min. The solution was then allowed to cool, giving a dark reddish precipitate which was filtered, washed with cold methanol and ether. Yield 90%. *Anal.* Calc. for $C_{24}H_{26}Cl_2Fe_2N_4O_4$: C, 46.7; H, 4.2; N, 9.1. Found: C, 46.3; H, 4.2; N, 9.0%.

Physical measurements

Microanalyses were performed by the Service de Microanalyse du Laboratoire de Chimie de Coordination, Toulouse. IR spectra were recorded on KBr discs with a Perkin-Elmer 983 spectrometer. Electronic spectra were obtained with a Cary 2390 spectrometer. The extinction coefficients ϵ are expressed in l mol^{-1} cm^{-1}. The presence of two metallic centres per ligand explains the high valucs of the d–d transitions. ^1H and ^{13}C NMR spectra were recorded at 295 K with a Bruker AC 200 spectrometer. All chemical shifts (^1H and ^{13}C) are given in ppm versus TMS. Magnetic susceptibility data were collected on powdered samples of the different compounds with use of a SQUID-based sample magnetometer on a QUANTUM Design model MPMS instrument. All data were corrected for diamagnetism of the ligands estimated from Pascal's constants [27] and for TIP.

Results and discussion

Synthesis

A diamine such as ethylenediamine readily reacts with ethyloxalate but no well defined product can be isolated from the reaction mixture. This is due to an extensive polymerization which can be avoided by preventing the terminal NH_2 groups from reacting with the ester function. This is easily obtained by making use of steric hindrance. Thus two moles of 1,2-diamino-2-methylpropane react with one mole of ethyloxalate to yield almost quantitatively *N*,*N*′-bis[(2-amino-2-methyl)propyl]oxamide (H_2L^1 in Fig. 2) which can be used as it is to complex metal ions or modified to obtain new ligands.

In spite of the steric constraint the reactivity of the terminal NH_2 residues remains large enough to allow their condensation with aldehydic groups. Indeed we succeeded in isolating H_4L^2 (Fig. 2) and four homodinuclear complexes which according to analytical data have to be formulated as $Cu^{II}(L^2)Cu^{II}$, $Ni^{II}(L^2)Ni^{II}$, $V^{IV}O(L^2)V^{IV}O$ and $ClFe^{III}(L^2)Fe^{III}Cl$.

All the dinuclear complexes show a great solubility in the majority of organic solvents, particularly CH_2Cl_2, acetone and DMSO. They are slightly soluble in methanol and insoluble in water, pentane and diethyl ether.

Attempts to grow single crystals suitable for X-ray diffraction studies have so far been unsuccessful but the structure of H_4L^2 and of its complexes may be deduced unambiguously from the chemical analysis and spectral data.

Spectroscopic studies

^1H and ^{13}C NMR spectroscopy afford a good characterization of H_2L^1, H_4L^2 and the diamagnetic complex $Ni(L^2)Ni$. The relevant data are quoted in Tables 1 and 2. The attributions are based on the chemical shift, intensity and multiplicity values. They are further supported by comparison with literature data for similar compounds [24] and by an internal comparison between H_2L^1, H_4L^2 and $Ni(L^2)Ni$.

With regard to the nature of the compounds the most significant features of the ^1H spectra concern the –NH, $-NH_2$ and –OH groups. In the case of H_2L^1, the simultaneous presence of a triplet at 8.53 ppm (N*H*) and a doublet at 3.14 ppm (C*H*$_2$) shows that the diamine has reacted with ethyloxalate through the less congested NH_2 group. As for H_4L^2, we note that the N*H* and C*H*$_2$ signals are still present while new signals attributable to O*H*, aromatic C*H* and imino C*H* protons are observed in accordance with the formation of a Schiff base via the NH_2 group of H_2L^1. The N*H* and O*H* signals are no longer present in the spectrum of the complex.

As expected, a common feature of the IR spectra of H_2L^1 and H_4L^2 is the presence of the characteristic amide bands [28] (Table 3). In addition, bands attributable to the salicylaldimine moiety (νOH, νCN, νCC_{arom}) are observed in the case of H_4L^2. The relevant IR absorptions of the four complexes are quoted in Table 4. The attributions are made according to literature data [29–31]. The four spectra lack any NH absorption, showing that the oxamide group coordinated the metal ions in a bis-deprotonated form. The broad band at *c* 2600 cm^{-1} in the H_4L^2 spectrum does not appear in the spectra of the complexes in accordance with coordination of the deprotonated phenol group. This is further supported by the presence of the related stretching mode νCO at about 1540 cm^{-1}. This high value is likely due to delocalization over the chelate ring which increases the bond order of the CO bond [29]. However, this value remains lower than that expected for a bridging phenolate oxygen [32]. Considering finally that the location of the oxamide ν_{as}CO and ν_sCO at *c*. 1650 and 1325 cm^{-1}, respectively, are characteristic of bridging oxamide, we may infer that, in the four complexes, the metal ions are coordinated to the imino nitrogen and phenolato oxygen atoms on the one hand and to the oxygen and nitrogen atoms of the bridging oxamide on the other hand.

The electronic spectrum of H_2L^1 comprises one strong band at 220 nm showing that no transition originating in the oxamide moiety occurs in the 230–700 nm region. The spectrum of H_4L^2 depends on the solvent. In CH_2Cl_2, three bands are observed at 315 (14 300), 254 (45 500) and 225 (81 700) nm while in CH_3OH five bands are clearly discernible at 400 (2400), 312 (8300), 280 (7000), 250 (27 600) and 220 (64 500) nm. This behaviour is strongly reminiscent of that previously reported [33] for different salicylaldimine derivatives. The bands appearing in CH_3OH at 400 and 280 nm are attributed to a quinoid tautomer while the bands centered at *c*. 315, 250 and 220 nm are regarded as

TABLE 1. ^1H NMR data: H_2L^1 and H_4L^2 ligands, nickel complex $Ni(L^2)Ni$

	CH_3	CH_2	CH	CH(arom.)	NH_2	NH	OH
H_2L^1	1.08(s)	3.14(d)			1.59(b)	8.53(t)	
H_4L^2	1.33(s)	3.48(d)	8.39(s)	7.33(m) 6.90(m)		7.36(t)	13.42(s)
$Ni(L^2)Ni$	1.46(s)	2.67(s)	7.10(s)	7.16(t) 7.01(d) 6.75(d) 6.53(t)			

s: singlet; d: doublet; t: triplet; b: broad; m: multiplet; arom: aromatic.

TABLE 2. ^{13}C NMR data: H_2L^1 and H_4L^2 ligands, nickel complex $Ni(L^2)Ni$

	CH_3	CH_2	CH	$C(CH_3)_2$	C(O)N	C(arom)	CH(arom)
H_2L^1	28.4	50.7		49.9	160.2		
H_4L^2	25.1	49.1	162.7	60.5	160.3	118.9 161.0	116.6 118.2 132.2 132.8
$Ni(L^2)Ni$	27.0	55.0	157.8	72.6	169.1	120.9 163.1	116.6 118.2 133.0 133.7

TABLE 3. Relevant IR absorption of the ligands

	νNH	νOH	A_I^a	νCN	νCC	A_{II}^a	A_{III}^a	A_{IV}^a	A_V^a
H_2L^1	~3300		1674			1527	1222	770	741
H_4L^2	3293	2600(br)^b	1660	1629	1582	1522	1225	772	738

^{a}Amide band. ^{b}br: broad.

TABLE 4. Relevant IR absorptions of the complexes

	ν_{as}CO	νCN	νCC	νCO^a	ν_sCO
$Cu(L^2)Cu$	1658	1626	1602	1535	1332
$Ni(L^2)Ni$	1669	1607		1534	1324
$VO(L^2)VO$	1645	1612	1599	1545	1330
$ClFe(L^2)FeCl$	1644	1610	1599	1545	1322

^{a}CO of the salicylaldimine moiety.

due to transitions of the intramolecularly hydrogen-bonded salicylaldiminato chromophore.

The spectrum of $Cu(L^2)Cu$ is similar to that of CuSalen [34, 35]. In both cases five bands are observed at about 560 (980), 374 (14 800), 285 (37 000), 245 (50 300) and 227 (43 000) nm. The band at 560 nm is attributable to a d–d transition characteristic of a copper(II) ion in a square planar environment [6, 24, 36]. The extinction coefficient of this absorption is somewhat higher than would be expected for a d–d transition but it is very likely that it borrows intensity from the intense band at 374 nm. The nature of this latter band is open to discussion. Keeping into consideration that it is observed for the anionic form of uncomplexed salicylaldimine derivatives and for various related complexes [29, 35, 37, 38], we feel that it is due to $\pi \rightarrow \pi^*$ transition within the salicylaldimine part of the ligand. However, it may be noted that a strong absorption is observed around 350 nm in the spectra of binuclear copper(II) complexes involving an oxamide bridge but devoided of any salicylaldimine residue [6]. The spectrum of $Ni(L^2)Ni$ displays four bands at 410 (1200), 340 (22 000), 360 (21 200) and 252 (70 500) nm. The 410 nm absorption is attributed to a d–d transition characteristic of a square planar Ni(II) ion [39]. Tentatively the bands at 340 and 360 nm are assigned to a ligand-to-metal charge transfer (LMCT) transition $\pi \rightarrow d_\sigma$ and intraligand $\pi \rightarrow \pi^*$ transition, respectively. In the case of $ClFe(L^2)FeCl$, owing to their location and intensity none of the detected absorptions (468 (4180), 329(sh) and 258 (33 400) nm) can have a d–d origin. From a literature survey [38, 40–42] it seems likely that the bands at 468 and 320 nm are LMCT transitions, $\pi \rightarrow d_\pi$ and $\pi \rightarrow d_\sigma$, respectively, the d–d transitions being likely obscured by the intense LMCT band at 468 nm.

Three d–d transitions are expected for a vanadium(IV) ion in a square-pyramidal environment, namely $d_{xy} \rightarrow d_{xz}$, d_{yz}(II), $d_{xy} \rightarrow d_{x^2-y^2}$(I) and $d_{xy} \rightarrow d_{z^2}$(III). The third transition is known to be very often obscured by CT transitions. In the spectrum of $VO(L^2)VO$, two well-resolved bands peaking at 540 (80) and 720 (38) nm may be attributed to (I) and (II), respectively. The shoulder appearing at 450 nm is a likely candidate for (III) while the fourth discernible band at 365 nm (9060) is thought to be due to a $\pi \rightarrow \pi^*$ transition [43]. It is noteworthy to compare bands (I) and (II) with those obtained with VOSalen [44] at 595 and 659 nm. If, in a first approximation, we admit that band (I) is related to the in-plane ligand field strength, the oxamide moiety in H_4L^2 strongly increases the strength of this field.

Magnetic properties

Let us recall first that $Ni(L^2)Ni$ is diamagnetic. As for $Cu(L^2)Cu$, it displays a magnetic behaviour characteristic of a strong antiferromagnetic interaction with very low values of χ_M at low temperature and a maximum of χ_M at temperature higher than room temperature. The experimental data corrected for diamagnetism are fitted to the Bleaney-Bowers relation. A satisfactory fit ($R=1.3\times10^{-3}$) is obtained with $g=2.10$ and $J=-560$ cm^{-1} (Fig. 3). This value is very similar to those reported for oxamide-bridged dicopper complexes [5–8, 24, 25] and supports the conclusion suggested by the analytical and spectroscopic data regarding the structure of the complex.

From 5 to 280 K, the thermal dependence of the susceptibility of VO(L^2)VO can be accurately represented by a simple Curie law with $C=0.69$ cm^3 K mol^{-1} leading to the conclusion that the magnetic interaction is, at the best, very feeble (Fig. 4). Dimeric complexes of V(IV) with *N*-(hydroxyalkyl)salicylaldimine have been reported [43, 46–49]. According to a recent structural study [49], they are formed by two monomeric units linked by alkoxide bridges which support a strong antiferromagnetic interaction between the two metal ions (J values varying from -150 to -520 cm^{-1}). On the contrary a ferromagnetic interaction ($J=+4.2$ cm^{-1}) has been evidenced for VOSalen infinite chains [50]. The absence of interaction in VO(L^2)VO is not unexpected. Unlike the related Cu(II) complex which has (x^2-y^2) type magnetic orbitals, the magnetic orbitals centred on the square-pyramidal V(IV) ions are of the *xy* type. An excellent pathway for exchange in the Cu(II) complex results from the fact that the (x^2-y^2) type orbitals point to the donor atoms of the bridge. In contrast the orbitals on the V(IV) ions are aligned and not directed at the bridging ligand donors. Therefore no important interaction can be mediated by the bridge. In principle, a direct σ overlap could be operative but the large separation between the two metal ions suggests this mechanism is not significant.

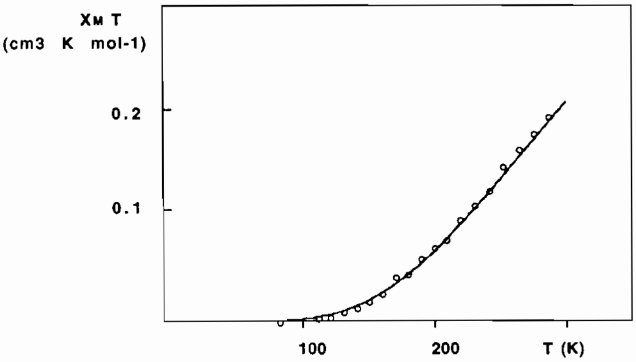

Fig. 3. Experimental (○) and calculated (——) temperature dependence of $\chi_M T$ for Cu(L^2)Cu.

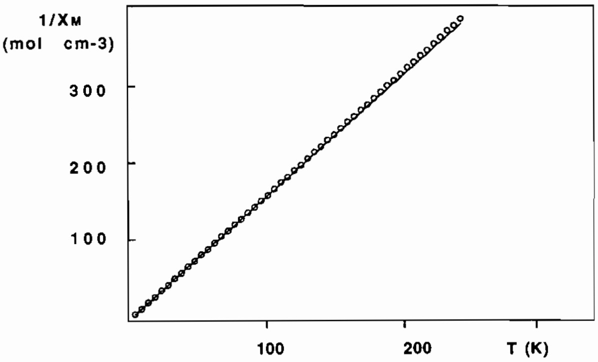

Fig. 4. Experimental (○) and calculated (——) inverse of the molar susceptibility vs. T for VO(L^2)VO.

As for ClFe(L^2)FeCl, the thermal variation of its molar magnetic susceptibility is shown in Fig. 5. The μ_{eff} value of 7.42 BM observed at 280 K substantiates the presence of high-spin Fe(III) ions. As μ_{eff} decreases on decreasing the temperature, there is an antiferrofjmagnetic interaction between the two $S=5/2$ ions leading to spin states with integer spin values, the ground state being a singlet ($S=0$). The theoretical equation for the corrected magnetic susceptibility of a dinuclear complex of this type incorporates four parameters: the exchange coupling J, the electronic factor g and the zero-field splitting factors D and E. In the present case a good fit to the experimental values is obtained by assuming that the fine-structure parameters are negligible so that the susceptibility is represented by [51]:

$$\chi=(2N\beta^2g^2/kT)(A/B)$$

with $A=x+5x^3+14x^6+30x^{10}+55x^{15}$
$B=1+3x+5x^3+7x^6+9x^{10}+11x^{15}$
and $x=\exp(J/kT)$

The quality of the fit below 10 K is improved by assuming the presence of a small amount (p) of an uncoupled (paramagnetic) impurity. The impurity is thought to be a mononuclear high-spin Fe(III) complex of the same molecular weight as one corresponding to the original complex and with a magnetic susceptibility obeying the Curie law ($\chi=35\ N\beta^2g^2/12kT$). Finally a good fit ($R=5.3\times10^{-4}$) is obtained over the whole

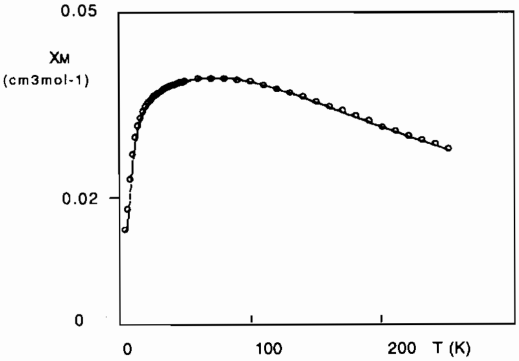

Fig. 5. Experimental (○) and calculated (——) temperature dependence of the magnetic susceptibility for ClFe(L^2)FeCl.

range of temperatures by adopting $p=0.6\%$, $g=2.1$ and $J=-9.5\ \mathrm{cm}^{-1}$.

To the best of our knowledge, there is no example in the literature of oxamidato-bridged dinuclear Fe(III) complexes. Three complexes have been reported [52, 53] in which the oxalate ligand couples two high-spin iron(III) ions with J values of $-7.0\pm0.2\ \mathrm{cm}^{-1}$. Our complex with a J value of $-9.5\ \mathrm{cm}^{-1}$ illustrates the superiority of oxamide over oxalate in supporting antiferromagnetic interaction.

Finally our data afford a new example of the great efficiency of Cu(II) to yield antiferromagnetic interactions compared to Fe(III). Taking into account the number (n) of unpaired electrons on each magnetic centre, we may compare the n^2J values [54, 55]. We have $-560\ \mathrm{cm}^{-1}$ for Cu(L^2)Cu and $-237.5\ \mathrm{cm}^{-1}$ for ClFe(L^2)FeCl.

Conclusions

To sum up the main results arising from this work, we would say that it is possible to prepare and isolate monomeric N,N′-disubstituted oxamides involving substituents with terminal NH_2 residues. The interest of this type of compound as precursors for original ligands is illustrated by the preparation of a new binucleating ligand which affords the first examples of vanadium(IV) and iron(III) oxamidato-bridged dinuclear complexes. Further works are in progress to prepare heterodinuclear complexes. Indeed, we have shown in a previous work that similar ligands with two identical coordination sites [25] are able to yield a mononuclear complex which can be isolated and act as a ligand toward a second metal centre. Such a possibility is due to the *cis–trans* isomerization of the oxamido group.

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