A dimeric Cu(II) acetate complex containing axially coordinated *p*-pyridyl nitronyl nitroxide radicals: $[Cu^{II}(CH_3COO)_2(NITpPy)]_2$†

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The synthesis, X-ray crystal structure, and magnetic behaviour of a new dimeric copper(II) compound, $[Cu^{II}(CH_3COO)_2(NITpPy)]_2$, is described. This compound presents a $Cu_2(COO)_4$ cage in which two copper atoms are linked by CH_3COO^- anions, yielding a short Cu–Cu distance of 2.6236(12) Å. *p*-Pyridyl nitronyl nitroxide radicals are localised in the apical positions. The magnetic study shows a strong antiferromagnetic Cu–Cu intradimer interaction and intermolecular antiferromagnetic interactions between the radical units at very low temperature. A Cu(II)–Cu(II) interaction parameter of $J = -321 \pm 1\ cm^{-1}$ was found.

Numerous dimeric Cu(II) compounds formulated as $[Cu^{II}X_2L]_2$, X = acetate, formate, silanecarboxylate, *etc.* and L = pyridine, quinoline and nitroxyl radicals, have been reported.[1–9] It has been found that in those compounds with non-magnetic L ligands, the strong antiferromagnetic spin coupling arises from an intramolecular interaction through the bridging ligands and the magnitude of the coupling strongly depends on the nature of these bridging ligands. Few examples of compounds containing paramagnetic nitroxide ligands have been reported.[9,10] In all cases the organic radicals are bonded to the metal through the oxygen atom of the nitroxide groups. For example, the tempo (2,2,6,6-tetramethyl-1-piperidinyloxy) adducts of Cu(II), trifluoro, trichloro and dibromoacetate, are diamagnetic in the temperature range 6–300 K as a result of intramolecular spin coupling between the radical and the copper atom. In the case of $Rh_2(X)_4(tempo)_2$ (X = η^2-perfluorocarboxylato anion as bridging ligand), it has been suggested that the strong antiferromagnetic interactions occur through the $Rh_2(X)_4$ core, whereas this type of interaction did not occur in the analogous compound containing Mo instead of Rh.[10] Finally, it has also been found that the nitroxyl-containing product can not be obtained when an unsubstituted bridging acetate ligand is employed.[9] The presence of one or more halogen substituents in the bridging ligand is necessary to obtain such dimeric Cu(II) compounds involving nitroxide radicals with NO–Cu coordination. The nitronyl nitroxide radical used in this work is NITpPy [2-(4′-pyridyl)-4,4,5,5-tetramethylimidazoline-1-oxyl 3-oxide]. It has been used as a bridging ligand between metal atoms in many magnetic materials, such as $Mn(hfac)_2(NITpPy)$[11] (hfac = hexafluoroacetylacetonato) and $[Cu(hfac)_2]_3(NITpPy)_2$,[12] with the spin residing on the d and p orbitals. In the first compound, the Mn sites are μ_2-bridged by the oxygen atoms of the nitroxide groups, while they are linked in the second one through both the nitrogen atom of the pyridyl ring and the oxygen atoms of the NO groups. We report here the synthesis, X-ray crystal structure and magnetic behaviour of $[Cu^{II}(_3COO)_2(NITpPy)]_2$, obtained with a unsubstituted acetate ligand and in which the NITpPy radicals are axially coordinated to the metal through the nitrogen atom of the *p*-pyridyl ring.

Experimental

Synthesis

$Cu(CH_3COO)_2 \cdot H_2O$ (Aldrich) was used as purchased. NITpPy was prepared as previously described.[13,14] All experiments were conducted under argon using freshly distilled solvents.

$[Cu^{II}(CH_3COO)_2(NITpPy)]_2$. $Cu(CH_3COO)_2 \cdot H_2O$ (0.200 g, 1 mmol) was dissolved in a mixture of 5 ml of ethanol and 1 ml H_2O and added to a 10 ml ethanol solution of NITpPy (0.468 g, 2 mmol), leading to a blue solution. A green precipitate deposited after stirring 1 h at 50 °C; this was filtered off and washed with ethanol. Elongated green parallelepiped crystals were obtained by slow evaporation of an acetonitrile solution. Crystals suitable for X-ray diffraction were grown over two weeks by slow diffusion of acetonitrile solutions of $Cu(CH_3COO)_2 \cdot H_2O$ and NITpPy in an H-shaped tube. Mp 234 °C, Anal. found (calc.) for $CuC_{16}H_{22}N_3O_6$: Cu 15.29 (15.28), C 46.50 (46.20), H 5.32 (5.33), N 10.12 (10.10%); IR (KBr): $\nu_{N\text{-}O}$ 1371 (s), 1138 (m); ν_{py} 1610 (m), 1547 (m), 1448 (m), 1404 (m) cm^{-1}.

Crystallographic data collection and structure determination

A single crystal was mounted on an Enraf–Nonius CAD4 diffractometer equipped with a graphite monochromated Mo-Kα radiation source ($\lambda = 0.71073$ Å). The air-sensitive

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Table 1 Crystal data and structure refinement for $[Cu^{II}(CH_3COO)_2(NITpPy)]_2$

Chemical formula	$Cu_2C_{32}H_{44}N_6O_{12}$
Formula weight	831.82
T/K	293(2)
Crystal system	Triclinic
Space group	$P\bar{1}$
a/Å	7.307(3)
b/Å	9.337(2)
c/Å	14.654(4)
α/°	101.79(2)
β/°	97.75(2)
γ/°	103.75(3)
u/Å^3	932.7(5)
Z	1
μ/mm^{-1}	1.208
Total reflections	4844
Unique reflections	4500 [R(int) = 0.0192]
Final R indices [$I > 2\sigma(I)$]	$R_1 = 0.0369$, $wR_2 = 0.0835$
R indices (all data)	$R_1 = 0.0787$, $wR_2 = 0.0962$

crystal was protected with glue. Cell dimensions and the orientation matrix for data collection were obtained from least-squares refinement, using the setting angles of 25 centred reflections. The crystal data are summarised in Table 1. The intensities were collected by $\theta - 2\theta$ scans; no significant decay was revealed on the three standard reflections measured every hour during data collection. Data reduction and correction was performed with MolEN.[15] Lorenz polarisation and semi-empirical absorption corrections (ψ-scan method)[16] were applied to the intensities of all data. Scattering factors and corrections for anomalous dispersion were taken from ref. 17. The structure was solved with SHELXS97 and refined with SHELXL97[18] by the full-matrix least-squares method on F^2.

CCDC reference number 440/212. See http://www.rsc.org/suppdata/nj/b0/b0044911/ for crystallographic files in .cif format.

Magnetic and spectroscopic measurements

Magnetic measurements down to 2 K were performed with a Quantum Design MPMS-5S SQUID magnetometer. All magnetic investigations were carried out on a polycrystalline sample. The molar susceptibility was corrected for the sample holder and for the diamagnetic contribution of all atoms by using Pascal's tables.[19]

IR characterisations were performed on a KBr pellet sample with an IR Bomem-Michelson 100 spectrometer.

Results and discussion

Crystal structure

An ORTEP drawing of the molecular structure is shown in Fig. 1. The molecule lies on an inversion centre. The $Cu_2(COO)_4$ core forms a cage in which the two copper atoms are linked by the CH_3COO^- anions, which act as bridging ligands. The Cu–Cu distance [2.6236(12) Å], the Cu–O bond lengths [mean value 1.965(2) Å], as well as the Cu–O–C and O–C–O bond angles (mean values 123.1 and 125.4°, respectively) are very close to those observed in related units with the same geometry.[5,7,8] In the centrosymmetric dinuclear Cu cage, the CH_3COO^- ligands are arranged so as to have approximately fourfold rotational symmetry along the Cu–Cu axis, with the O–Cu–O bond angles between neighbouring bridges ranging from 88.7(1) to 90.7(1)°. Each copper atom adopts a deformed square pyramidal geometry in which the metal centre is displaced 0.201(1) Å out of the plane formed by the four oxygen atoms of the acetates. Each NITpPy unit is axially coordinated to a copper atom through the nitrogen

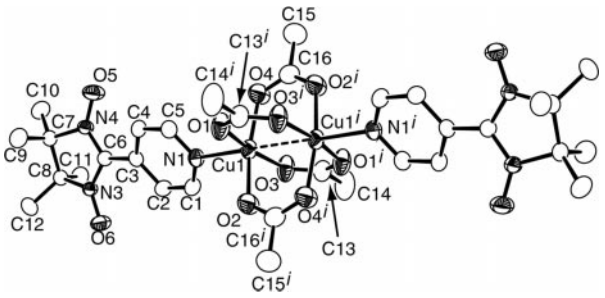

Fig. 1 ORTEP drawing with 50% ellipsoid probability showing atom labelling of $[Cu^{II}(CH_3COO)_2(NITpPy)]_2$. Symmetry transformation used to generate equivalent atoms: ^{i} $1-x$, $1-y$, $1-z$.

atom of the pyridyl ring with a Cu–N bond length of 2.173(2) Å and O–Cu–N angles ranging from 95.4(1) to 96.3(1)°. The dihedral angle between the pyridyl ring and the plane defined by two acetate bridges O1–C13^i–C14^i–O3^i opposite each other is 38.9(1)°, that between the ON–C–NO moieties and the pyridyl ring is 25.97(7)°. Selected bond distances and bond angles are summarised in Table 2.

The shortest intermolecular distances involving the NO moieties of the nitronyl nitroxide groups are O5···O5 = 3.721(5) and O6···O6 = 4.321(4) Å (see Fig. 2). Along the a axis, the shortest distance is O5···O6 = 4.033(3) Å; the shortest oxygen methyl distance is O5···C11 = 3.333(4) Å.

Magnetic properties

In principle, two different interactions between the spin carriers in $[Cu(CH_3COO)_2(NITpPy)]_2$ can be anticipated: one between a Cu(II) ion and its organic radical ligand, and a second between the two Cu(II) centres. However, the strengths of these interactions should be very different. Indeed, the interaction between Cu(II) ions bridged by acetate type ligands is well documented to be of the order of several hundreds of cm^{-1}, whereas the coupling between the nitronyl nitroxide radical and Cu(II) through the pyridine unit is more than one order of magnitude smaller.[12,20] In the reported compound the paramagnetic ligand is located at the axial position of the coordination sphere of the Cu(II); this should even decrease their magnetic exchange because the d_{z^2} orbital involved in the bonding does not contain the unpaired electron of the metal centre. Finally, the rather short intermolecular distances between the nitronyl nitroxide units might also lead to weak intermolecular interactions.

The temperature dependence of the molar magnetic susceptibility, χ_M, of $[Cu(CH_3COO)_2(NITpPy)]_2$ was investigated in

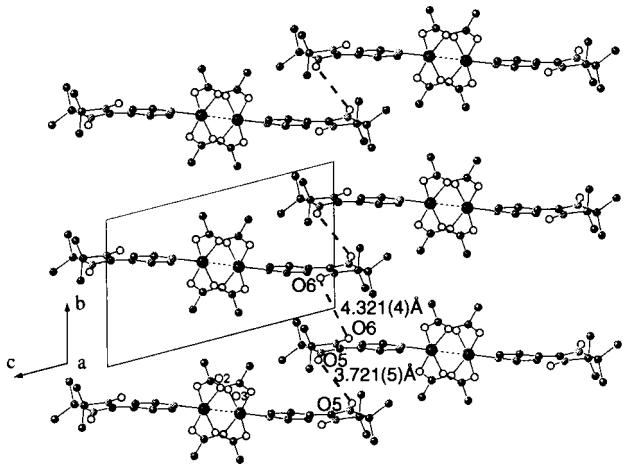

Fig. 2 Projection of the crystal structure in the bc plane showing the shortest intermolecular distances involving the NO moieties O5–O5 = 3.721(5) Å, O6–O6 = 4.321(4) Å.

Table 2 Selected bond lengths and angles (Å, °) for $[Cu^{II}(CH_3COO)_2(NITpPy)]_2$. Symmetry transformation used to generate equivalent atoms: ^{i} $1-x+1, 1-y+1, 1-z+1$

Cu1–Cu1^i	2.6236(12)	C16–C15	1.499(4)
Cu1–O2	1.960(2)	C16–O4	1.250(3)
Cu1–O1	1.964(2)	C16–O2^i	1.253(3)
Cu1–O3	1.966(2)	N3–O6	1.266(3)
Cu1–O4	1.971(2)	N3–C6	1.343(3)
Cu1–N1	2.173(2)	N4–O5	1.272(3)
C13–C14	1.504(4)	N4–C6	1.351(3)
C13^i–O1	1.251(3)	C6–C3	1.464(3)
C13–O3	1.249(3)		
O1–Cu1–O2	89.38(10)	O6–N3–C8	121.54(18)
O1–Cu1–O4	88.74(10)	C13–O3–Cu1	123.52(18)
O2–Cu1–O3	90.68(10)	O3–C13–O1^i	125.6(3)
O3–Cu1–O4	88.81(10)	O3–C13–C14	116.9(3)
O1–Cu1–N1	96.19(8)	O1^i–C13–C14	117.5(3)
O1–Cu1–Cu1^i	84.56(6)	C13–O1–Cu1^i	122.58(19)
N1–Cu1–Cu1^i	179.21(6)	C16–O2^i–Cu1^i	124.3(2)
O5–N4–C7	121.89(19)	O4–C16–O2^i	125.2(3)
O5–N4–C6	126.8(2)	O4–C16–C15	118.1(3)
N3–C6–N4	108.87(19)	O2^i–C16–C15	116.7(3)
O6–N3–C6	126.88(19)	C16–O4–Cu1	122.14(18)

the temperature range 2–300 K. The plot of $\chi_M T$ *vs.* T is shown in Fig. 3. At room temperature, $\chi_M T$ is equal to 1.15 cm^3 K mol^{-1}, a value lower than that expected for four non-correlated $S = 1/2$ spin carriers. As the temperature is lowered, $\chi_M T$ gradually decreases to reach a plateau value of 0.75 cm^3 K mol^{-1} between 30–100 K, then drops sharply below 30 K to 0.15 cm^3 K mol^{-1} at 2 K. The profile of this curve indicates that the anticipated strong antiferromagnetic interaction takes place between the Cu(II) ions. This interaction tends to cancel the magnetic moments of the metal centres, leading to a molecular unit with only the two nitronyl nitroxide units remaining as uncorrelated spin carriers below 100 K. The experimental data in the temperature range 50–300 K could be fairly well reproduced by a dimer-type model: $H = -J\ \boldsymbol{S}_1 \cdot \boldsymbol{S}_2$ (solid line, Fig. 3).[19c] The best fit parameter obtained is $J = -321 \pm 1$ cm^{-1} with g fixed to 2.0. The magnitude of the exchange interaction, as measured by the J value, is dependent on the atom that is directly bonded to the bridging carboxylato group. For acetate, the observed value of J is similar to those observed in other dimeric copper(II) compounds, $J = -330$ cm^{-1}.[5,6] The decrease of $\chi_M T$ at lower temperatures is attributed to intermolecular antiferromagnetic interactions between the radical units. The occurrence of these antiferromagnetic interactions is also demonstrated by the χ_M *vs.* T plot, which exhibits a maximum at 3.5 K (insert, Fig. 3). Attempts to reproduce the low temperature behaviour by a dimer model did not lead to a satisfactory fit to the experimental data. This suggest that the intermolecular interaction involves more than just the two closest aminoxyl units as indicated by the shortest distances.

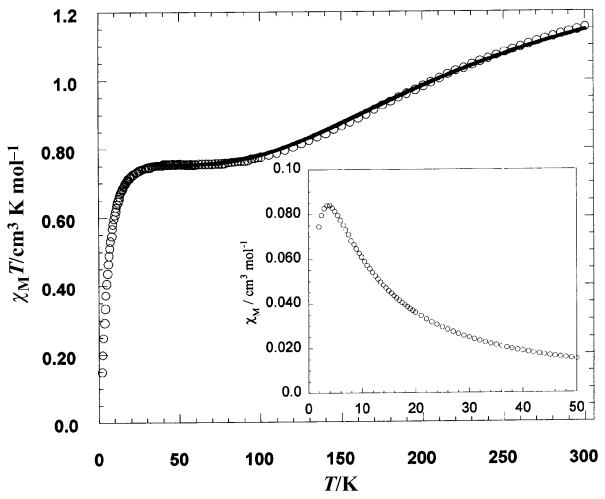

Fig. 3 Experimental and calculated (——) $\chi_M T$ *vs.* T curve for $[Cu(CH_3COO)_2(NITpPy)]_2$. The insert is an expanded view of the χ_M *vs.* T curve showing the maximum in χ_M.

Conclusion

A new dimeric Cu(II) acetate complex containing axially coordinated paramagnetic *p*-pyridyl nitronyl nitroxide radicals has been synthesised and structurally and magnetically characterised. The magnetic properties reveal a strong intradimer antiferromagnetic interaction between the Cu(II) ions and at very low temperatures a weak intermolecular antiferromagnetic interaction between the nitroxide radicals is present. In agreement with the experimental magnetic data, preliminary theoretical calculations found a singlet ground state.

References and notes

1 R. J. Doedens, *Prog. Inorg. Chem.*, 1976, **21**, 209.
2 Y. Muto, A. Sasaki, T. Tokii and M. Nakashima, *Bull. Chem. Soc. Jpn.*, 1985, **58**, 2572.
3 M. Yamanaka, H. Uekusa, S. Ohba, Y. Saito and S. Iwata, *Acta Crystallogr., Sect. B*, 1991, **47**, 344.
4 H. Uekusa, S. Ohba, T. Tokii, Y. Muto, M. Kato, S. Husebye, O. W. Steward, S.-C. Chang, J. P. Rose, J. F. Pletcher and I. Suzuki, *Acta Crystallogr., Sect. B*, 1992, **48**, 650.
5 O. W. Steward, R. C. McAfee, S.-C. Chang, S. R. Piskor, W. J. Schreiber, F. Jury, C. E. Taylor, J. F. Pletcher and C.-S. Chang, *Inorg. Chem.*, 1986, **25**, 771.
6 A. Harada, M. Tsuchimoto, S. Ohba, K. Iwasawa and T. Tokii, *Acta Crystallogr., Sect. B*, 1997, **53**, 654.
7 M. Goto, Y. Kani, M. Tsuchimoto, S. Ohba, H. Matsushima and T. Tokii, *Acta Crystallogr., Sect. C*, 2000, **56**, 7.
8 H. Nakagawa, Y. Kani, M. Tsuchimoto, S. Ohba, H. Matsushima and T. Tokii, *Acta Crystallogr., Sect. C*, 2000, **56**, 12.
9 L. C. Porter, M. H. Dickman and R. J. Doedens, *Inorg. Chem.*, 1986, **25**, 678.
10 T. R. Felthouse, T.-Y. Dong, D. N. Hendrickson, H.-S. Shieh and M. R. Thompson, *J. Am. Chem. Soc.*, 1986, **108**, 8201.
11 (*a*) A. Caneschi, D. Gatteschi, P. Rey and R. Sessoli, *Inorg. Chem.*,

1988, **27**, 1756; (*b*) A. Caneschi, D. Gatteschi, J. P. Renard, P. Rey and R. Sessoli, *Inorg. Chem.*, 1989, **28**, 1976; (*c*) A. Caneschi, D. Gatteschi, R. Sessoli and P. Rey, *Acc. Chem. Res.*, 1989, **22**, 392.
12 A. Caneschi, F. Ferraro, D. Gatteschi, P. Rey and R. Sessoli, *Inorg. Chem.*, 1991, **30**, 3162.
13 (*a*) E. F. Ulman and R. H. Holm, *J. Am. Chem. Soc.*, 1970, **82**, 2979; (*b*) M. S. Davis, K. Morokuma and R. W. Kreilick, *J. Am. Chem. Soc.*, 1972, **94**, 5588.
14 E. F. Ullman, L. Call and J. H. Osiecki, *J. Org. Chem.*, 1970, **35**, 3623.
15 MolEN, Enraf–Nonius, Delft, The Netherlands, 1990.
16 A. C. T. North, D. C. Philips and F. S. Mathews, *Acta Crystallogr., Sect. A*, 1968, **24**, 351.
17 *International Tables for X-Ray Crystallography*, ed. A. J. C. Wilson, Kluwer Academic Publishers, Dordrecht, The Netherlands, 1992, vol. C.
18 G. M. Sheldrick, SHELXL 97, Program for the Refinement of Crystal Structures, University of Göttingen, Germany, 1997.
19 For diamagnetic contributions, see: (*a*) P. W. Selwood, *Magnetochemistry*, Interscience Publishers, New York, 1956; (*b*) F. E. Mabbs and D. J. Machin, *Magnetism and Transition Metal Complexes*, Chapman and Hall, London, 1973; (*c*) O. Kahn, *Molecular Magnetism*, VCH Publishers, New York, 1993.
20 A. Caneschi, F. Ferraro, D. Gatteschi, P. Rey and R. Sessoli, *Inorg. Chem.*, 1990, **29**, 1756.