PERGAMON

Polyhedron 21 (2002) 457–464

POLYHEDRON
www.elsevier.com/locate/poly

2-Anilinopyridinate of Cu(I) and adducts of 2-anilinopyridine and metal acetates.
Crystal structure of $Cu_2(\mu\text{-}OAc)_4(PhNHpy)_2$

José M. Seco [a], María J. González Garmendia [a,*], Elena Pinilla [b,c], María R. Torres [b]

[a] *Grupo de Química Inorgánica, Facultad de Ciencias Químicas, Universidad del País Vasco, UPV/EHU, Apartado 1072, E-20080 San Sebastian, Spain*
[b] *Laboratorio de Difracción de Rayos-X, Facultad de Ciencias Químicas, Universidad Complutense, E-28040 Madrid, Spain*
[c] *Departamento de Química Inorgánica, Facultad de Ciencias Químicas, Universidad Complutense, E-28040 Madrid, Spain*

Received 17 July 2001; accepted 6 December 2001

Abstract

The adducts of $M(OAc)_2{\cdot}nH_2O$ (M = Cu, Co, Ni, Zn) with 2-anilinopyridine, $M(OAc)_2(PhNHpy)$, have been synthesized and characterized. The X-ray crystal structure of $Cu_2(\mu\text{-}OAc)_4(PhNHpy)_2$ shows the dimer structure of $Cu_2(\mu\text{-}OAc)_4(H_2O)_2$ with the PhNHpy ligand in the axial positions of the water molecules. It is antiferromagnetic ($2J = -286$ cm^{-1}). Signals of the triplet state are observed in its EPR spectrum and the zero field splitting parameter ($D = 0.33$ cm^{-1}) has been calculated. The electronic spectra and the strong antiferromagnetism of the cobalt ($2J = -324$ cm^{-1}) and nickel ($2J = -382$ cm^{-1}) compounds allow to propose also a dimeric structure for them. By excess of ligand, in the anionic form, the Cu(I) compound Cu(PhNpy) was obtained for which a dinuclear structure with a lineal coordination in Cu(I) is proposed.

Keywords: 2-Anilinopyridine; Crystal structures; Antiferromagnetic dimers; Dinuclear acetates; Copper(I)

1. Introduction

The dinuclear copper(II) acetate dihydrate $[Cu_2(\mu\text{-}OAc)_4(H_2O)_2]$, with four bridging acetate groups and the water molecules in the axial positions, is one of the most studied dinuclear compounds of Cu(II) in the structural and magnetic aspects [1,2]. Also the adducts $[Cu_2(\mu\text{-}OAc)_4L_2]$ and $[Cu_2(\mu\text{-}O_2CR)_4L_2]$ with different ligands in the axial positions [3–6].

The hydrated acetates of cobalt(II) and nickel(II), $M(OAc)_2{\cdot}4H_2O$, are monomers and isostructurals [7]. The acetate groups are monodentate and two of them are coordinated to each metal atom. The octahedral coordination is completed by four water molecules. Intermolecular hydrogen bonds between non-coordinated oxygen atoms of the acetate groups and hydrogen atoms of water are involved in a tridimensional net. They have normal magnetic moments at room temperature. Among the carboxylate complexes of Co(II) and Ni(II) the dimer structures as that of $[Cu_2(\mu\text{-}OAc)_4L_2]$ are infrequent. The X-ray diffraction has confirmed this structure in $[M_2(\mu\text{-}O_2CPh)_4(quin)_2]$, for quin = quinoline and M = Co(II) [8] and Ni(II) [9]. These complexes are antiferromagnetic, unlike other compounds with the same components but different structure, as $[Co_3(O_2CPh)_6(quin)_2]$ [10].

In $Zn(OAc)_2{\cdot}2H_2O$ two bidentate acetate anions and two water molecules are coordinated to the zinc atom [11]. The hydrogen bonds are established in a bidimensional net.

The 2-anilinopyridine, (*N*-phenyl-2-pyridinamine, PhNHpy), is an asymmetrical ligand, with two nitrogen atoms in the 1,3 positions, which can coordinate as monodentate or bidentate. As monodentate ligand the coordination is established through the pyridinic nitrogen and as anionic bidentate through both nitrogen atoms [12,13]. In previous papers we reported the reaction between $[Cu_2(NN)_2(\mu\text{-}OH)_2]X_2{\cdot}nH_2O$, where *NN* = 2,2′-bipyridyl or 1,10-phenanthroline and X^- =

---

* Corresponding author. Tel.: +34-943-018208; fax: +34-943-212236.
E-mail address: qppgogam@sq.ehu.es (M.J. González Garmendia).

0277-5387/02/$ - see front matter © 2002 Elsevier Science Ltd. All rights reserved.
PII: S0277-5387(01)01015-4

PF_6^- or CLO_4^-, and PhNHpy. For $X^- = PF_6^-$ [14] each PhNHpy molecule is coordinated to a copper atom through the pyridinic nitrogen and the hydrogen bonded to the anilinic nitrogen is involved in an hydrogen bond with the oxygen atom of a bridging OH group. When $X^- = ClO_4^-$ [15] the ligand interacts with the medium (methanol) and a methylene group is inserted between the anilinic nitrogen atom and the bridging oxygen. The corresponding magneto–structural correlations were established for the resulting dinuclear complexes.

In this paper we describe the interaction between PhNHpy and the $M(OAc)_2 \cdot nH_2O$ acetates (M = Cu, Co, Ni, Zn). The scope of substitution of AcO^- by the anionic ligand $PhNpy^-$ was unsuccessful and the Cu(I) compound CuPhNpy was obtained. The other adducts of PhNHpy, $M(OAc)_2(PhNHpy)$ were obtained. Crystal structure of Cu(II) compound has been determined. Electronic spectra and magnetic and EPR results are also described and allow to make a structural proposition.

2. Experimental

2.1. Synthesis

The anionic form of PhNHpy was prepared, in situ. The ligand was dissolved in the minimal volume of absolute EtOH and metallic Na, in stoichiometric proportion, was added. The mixture was allowed to stand 15 min before using it [16].

2.1.1. Cu(PhNpy) (**1**)

A solution of anionic PhNHpy (5 mmol) in absolute EtOH (10 ml) was added to a solution of $Cu(OAc)_2 \cdot H_2O$ (1 mmol) in MeOH (30 ml). The mixture was refluxed for 3 h and cooled at room temperature (r.t.). A yellow precipitate was formed. It was filtered off, washed with MeOH and dried by air suction.

Yield: 83%. m.p. (dec.) 262 °C. *Anal.* Found: C, 56.6; H, 3.9; Cu, 27.6; N, 11.9. Calc. for $C_{11}H_9CuN_2$: C, 56.8; H, 3.9; Cu, 27.3; N, 12.0%. Soluble in C_6H_6 and CH_2Cl_2 under nitrogen and slightly soluble in dimethylformamide.

2.1.2. $Cu(OAc)_2(PhNHpy)$ (**2**)

A solution of PhNHpy (0.34 g, 2 mmol) in THF (10 ml) was added to $Cu(OAc)_2 \cdot H_2O$ (0.20 g, 1 mmol) in THF (40 ml). The solution was stirred during 2 h and a precipitate was formed. The blue green precipitate was filtered off, washed with THF and dried in vacuo over $CaCO_3$.

Yield: 80%. m.p. (dec.) 262 °C. *Anal.* Found: C, 51.7; H, 4.5; Cu, 17.9; N, 7.7. Calc. for $C_{15}H_{16}CuN_2O_4$: C, 51.2; H, 4.6; Cu, 18.0; N, 8.0%. Soluble in dimethylformamide, $C_6H_5NO_2$, nitromethane and partially soluble in $CHCl_3$ and MeOH.

2.1.3. $M(OAc)_2(PhNHpy)$, M = Co (**3**), Ni (**4**), Zn (**5**)

These complexes were synthesized according to the method described by Brookes and Martin [17] for the reaction of NiOAc with azaindole. A solution of PhNHpy (0.68 g, 4 mmol) in MeOH (10 ml) was added to a solution of $M(OAc)_2 \cdot nH_2O$ (2 mmol) in MeOH (40 ml). The solution was stirred during 5 min and was concentrated to dryness in the rotavapor. The product was of colour garnet for Co, green for Ni and white for Zn. It was dissolved in $C_6H_5CH_3$ and heated at 100 °C during 45 min (30 min for the Zn compound). The precipitate formed was filtered off, washed with $C_6H_5CH_3$ and dried by air suction.

*Compound **3**:* Dark green powder. Yield: 79%. m.p. (dec.) 215 °C. *Anal.* Found: C, 51.8; H, 4.4; N, 8.5. Calc. for $C_{15}H_{16}CoN_2O_4$: C, 51.9; H, 4.6; N, 8.1%. Soluble in $C_6H_5NO_2$. Soluble in dimethylformamide, MeOH, EtOH and C_3H_6O with colour change from green to garnet. Partially soluble in $CHCl_3$.

*Compound **4**:* Light green powder. Yield: 60%. m.p. (dec.) 209 °C. *Anal.* Found: C, 51.2; H, 4.5; N, 78.3; Ni, 17.3. Calc. for $C_{15}H_{16}N_2NiO_4$: C, 51.9; H, 4.6; N, 8.1; Ni, 16.7%. Soluble in dimethylformamide and $C_6H_5NO_2$ and partially soluble in MeOH, EtOH and $CHCl_3$.

*Compound **5**:* White powder. Yield: 87%. m.p. (dec.) 172 °C. *Anal.* Found: C, 50.5; H, 4.4; N, 7.6; Zn, 18.7. Calc. for $C_{15}H_{16}N_2O_4Zn$: C, 50.9; H, 4.6; N, 7.9; Zn, 18.4%. Soluble in dimethylformamide, $C_6H_5NO_2$, MeOH and $CHCl_3$ (partially).

2.2. Measurements

C, H and N were analysed in a Perkin–Elmer 240C Elemental Analyser. Copper, Ni and Zn were measured with an Atomic Absorption Spectrophotometer Perkin–Elmer 2380, $\lambda = 324.8$, 232.0 and 213.9 nm, respectively. Melting points were measured on an Electrothermal 9300. Conductivity measurements were made using a Metrhom E518 conductometer. IR spectra were recorded on a Nicolet FT-IR 510 spectrometer in the range 4000–400 cm^{-1} using KBr pellets and on a Nicolet 740 in 650–50 cm^{-1} range using nujol on a polyethylene film. Mass spectrum was obtained on an VG Autospec instrument with the liquid secondary ion mass spectra technique (LSISM), using nitrobenzyl alcohol as matrix with the addition of trifluoroacetic acid. Cs^+ cations at 30 Kv were used. Electronic spectra were recorded on a Shimadzu UV-265 FW spectrophotometer.

Magnetic measurements were carried out with a magnetometer Manics DSM-8 or a SQUID MPMSXL of

Quantum Design. Diamagnetic corrections have been applied [2]. The EPR spectra were recorded on a Bruker ESP 300 spectrometer with a Bruker ER 035 M gaussmeter, and HP 5325B frequency counter.

2.3. Crystal structure determination

Prismatic single crystals of $C_{30}H_{32}Cu_2N_4O_8$ (**2**) were grown by layering MeOH solution of copper(II) acetate dihydrate, MeOH and ether solution of 2-anilinopyridine. The X-ray diffraction data were collected, at 296 K, on a Bruker Smart CCD diffractometer, with graphite-monochromated Mo Kα radiation ($\lambda = 0.71073$ Å), operating in the ω and φ scanning mode. A summary of the crystallographic data, conditions used for the data collection and some refinement data are listed in Table 1.

Table 1
Crystallographic and structure refinement data for $[Cu_2(\mu\text{-}O_2CCH_3)_4(PhNHpy)_2]$ (**2**)

Empirical formula	$C_{30}H_{32}Cu_2N_4O_8$
Formula weight	703.68
Temperature (K)	296(2)
Wavelength (Å)	0.71073
Crystal system	monoclinic
Space group	$P2_1/n$
Unit cell dimensions	
a (Å)	11.3622(12)
b (Å)	7.5900(8)
c (Å)	17.9726(19)
β (°)	101.093(2)
V (Å^3)	1521.0(3)
Z	2
D_{calc} (g cm^{-3})	1.536
Absorption coefficient, μ (mm^{-1})	1.455
F (000)	724
Crystal size (mm)	$0.20 \times 0.20 \times 0.40$
θ Range for data collection (°)	1.96–23.29
Index ranges	$(-12, -8, -19)$ to (11, 7, 19)
Reflections collected	6446
Independent reflections	2188 ($R_{int} = 0.0448$)
Completeness to $\theta = 23.29°$ (%)	99.6
Absorption correction	None
Refinement method	full-matrix least-squares on F^2
Data/restraints/parameters	2188/0/209
Final R indices [$I > 2\sigma(I)$]	$R_1 = 0.0365$ (obs. 1545)
R indices (all data)	$wR_2 = 0.0893$
Goodness-of-fit on F^2	0.904
Maximum residual (e^{-3})	0.39

$R_1 = \Sigma(|F_o| - |F_c|)/\Sigma|F_o|$; $wR_2 = \{\Sigma[w(F_o^2 - F_c^2)^2]/\Sigma[w(F_o^2)^2]\}^{1/2}$.

Table 2
Mass spectra results for Cu(PhNpy) (**1**), (L = PhNpy)

m/z	Ion	Relative intensity (%)
465	$Cu_2L_2 + 1$	3
403	$CuLLH + 1$	42
233	$CuL + 1$	75
171	$LH + 1$	100
78	py^{+1}	13
63	Cu^{+1}	8

Data were collected over and hemisphere of the reciprocal space by combination of the three exposure sets. Each exposure of 20 s covered 0.3 in ω. The first 50 frames were collected at the end of the data collection to monitor crystal decay. No appreciable drop in the intensities of standard reflections was observed.

The structure was solved by Patterson (Cu atoms) and conventional Fourier techniques and refined by full-matrix least-squares on F^2 [18]. All atoms were refined anisotropically. Hydrogen atoms were included in calculated positions and refined riding on the respective carbon atoms, with some exceptions. H(2) has been located in a Fourier synthesis, included and riding on a N bonded atom.

3. Results and discussion

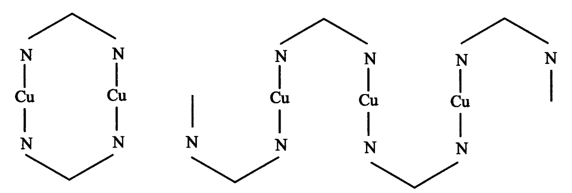
3.1. Characterization

The molar conductivity values for **1** in dimethylformamide and for **2**–**5** in methanol correspond to non-ionic compounds. The most significant band in the IR spectra is that assigned to the stretching ν(N–H) at approximately 3300 cm^{-1}. In compound **1** this band is not observed. This result confirms the presence of the anion PhNpy$^-$. In compounds **2**–**5** this band appears between 3274 and 3312 cm^{-1}, indicating the neutral form of the ligand.

In Table 2 are registered the mass spectra results for the Cu(I) compound. They agree with the dimeric structure of **1**. The most intense signals are those of LH + 1, CuL + 1 and CuLLH + 1, which can be generated in the matrix, from the dimer Cu_2L_2. The spectrum exhibits some signals for a mass higher than that of the dimer, but of very low intensity ($< 1\%$). The corresponding cations can be due to molecular associations.

The electronic spectrum of **1** shows the ligand band at 280 nm and no d → d transition bands. The yellow colour is due to charge transfer. The compound is diamagnetic.

According to the coordination possibilities of the ligand and the ligand–metal ratio, the compound **1** may present a dimeric or a linear chain structure (Scheme 1). In both cases the Cu(I) cation adopts a linear coordination and the ligand, in the anionic form, acts as bridging bidentate through pyridine and aniline nitrogen atoms. The dimeric structure has been found in $[Cu_2(dab)_2]$ (dab = diazoaminobenzene) [19], $[Cu_2(form)_2]$ (form = N,N'-di-p-tolylformamidinato) [20] and $[Cu_2(hpp)_2]$ (hppp = 1,3,4,6,7,8-hexahydro-2H-



Scheme 1. Dimer and linear chain disposition for Cu(PhNpy) (**1**).

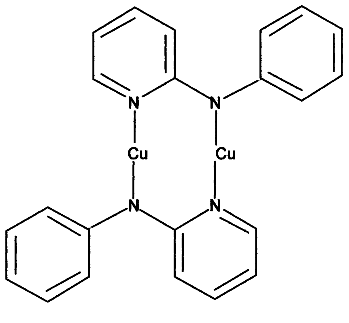


Fig. 1. Proposed structure for Cu(PhNpy) (**1**).

pyrimido[1,2-a]pyrimidinate) [21a]. In all three cases an eight members ring is formed, with a short Cu···Cu distance (2.45–2.50 Å) attributed to a combination of strong Cu–N bonding (1.86–1.94 Å) and very short bite distance for the ligands. In the ligand $PhNpy^-$ the relative position of the coordinating nitrogen atoms is the same that in the reported complexes and a similar dimeric structure is proposed (Fig. 1). The chain structure will be hindered by the steric effects between pyridine and phenyl groups of neighbouring ligands. The same dimeric structure has been proposed for $[Cu_2(MeNpy)_2]$ [21b].

3.2. Crystal structure of $[Cu_2(\mu\text{-}OOCCH_3)_4(PhNHpy)_2]$ (2)

Compound **2** consists of centrosymmetric dinuclear units, similar to other copper acetate derivates, in which four acetate groups are bridging the two copper atoms and a PhNHpy neutral ligand occupies the axial position of each copper atom, coordinated to them through the pyridine nitrogen atom. Fig. 2 shows an ORTEP view of the dimer geometry with 35% probability ellipsoids that includes the atom labelling. The hydrogen atoms have been omitted for clarity, only H(2) involved in an hydrogen bond is included. Selected interatomic distances and angles are listed in Table 3.

Each copper atom has a distorted square-planar pyramidal coordination, with four oxygen atoms in a plane, at an average distance of 1.971(3) Å; the fifth coordination position is occupied by the pyridine nitrogen, N(1), of a ligand molecule at 2.186(3) Å. The copper atom rises from the basal plane to the apical N(1) atom by 0.209(0.001) Å. The Cu···Cu separation is 2.6479(9) Å. The hydrogen atom, H(2), bonded to the anilinic nitrogen, N(2), is involved in an hydrogen bond to the oxygen, O(1), of an acetate group. Only two of the four acetate groups are involved in hydrogen bond.

The results are similar to those found for $[Cu_2(\mu\text{-}OAc)_4(H_2O)_2]$ [2] and other complexes, as the polymeric adduct of copper(II) acetate with 2-amonipyrimidine [22]. Hydrogen bonds of PhNHpy have been before described [12,14].

3.3. Electronic spectra

The dimethylformamide solution and diffuse reflectance spectral data are summarized in Table 4. The π → π* band on the ligand, at 274 nm, which in the reflectance spectra presents a broad absorption in the 360–190 nm range, is reproduced in all the complexes.

For $[Cu_2(\mu\text{-}OAc)_4(PhNHpy)_2]$ in solution, the three expected bands are observed: (a) 700 nm for the d → d transitions; (b) 360 nm, characteristic of copper acetate dimer structure and which is not observed in analogue monomers; and (c) 300 nm for charge transfer [23,24].

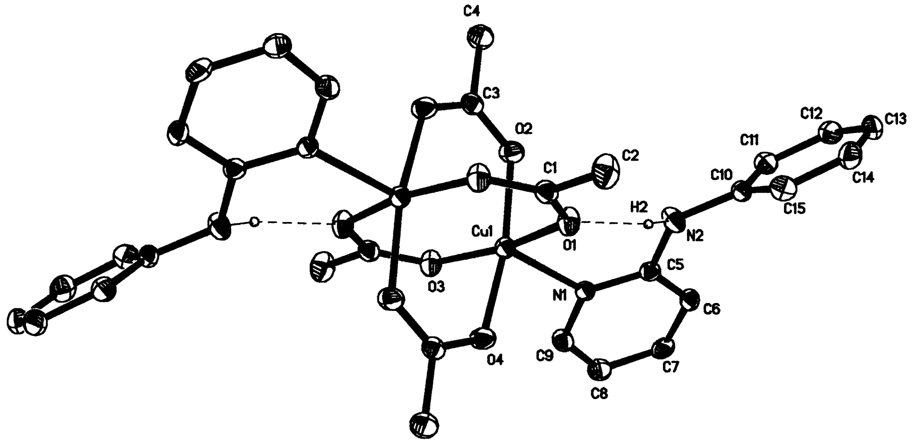


Fig. 2. ORTEP view of $[Cu_2(\mu\text{-}OAc)_4(PhNHpy)_2]$ (**2**).

Table 3
Selected interatomic distances (Å) and angles (°) for [Cu_2(μ-$OOCCH_3)_4(PhNHpy)_2$] (**2**)

Interatomic distances	
Cu(1)–O(2)	1.969(3)
Cu(1)–O(4)	1.964(3)
Cu(1)–O(3)	1.976(3)
Cu(1)–O(1)	1.974(3)
Cu(1)–N(1)	2.186(3)
Cu(1)···Cu(1)*	2.6479(9)
O(1)–C(1)	1.268(5)
N(1)–C(5)	1.349(5)
N(1)–C(9)	1.344(5)
C(1)–C(2)	1.499(6)
O(2)–C(3)	1.252(5)
N(2)–C(5)	1.385(5)
N(2)–C(10)	1.417(5)
C(3)–C(4)	1.505(6)
C(5)–C(6)	1.400(5)
C(6)–C(7)	1.371(6)
C(7)–C(8)	1.385(6)
C(8)–C(9)	1.359(6)
C(10)–C(11)	1.383(6)
C(10)–C(15)	1.392(6)
C(11)–C(12)	1.391(6)
C(12)–C(13)	1.376(6)
C(13)–C(14)	1.373(6)
C(14)–C(15)	1.376(6)
Bond angles	
O(2)–Cu(1)–O(4)	167.6(1)
O(2)–Cu(1)–O(3)	89.4(1)
O(4)–Cu(1)–O(3)	90.0(1)
O(2)–Cu(1)–O(1)	88.4(1)
O(4)–Cu(1)–O(1)	89.5(1)
O(3)–Cu(1)–O(1)	168.0(1)
O(2)–Cu(1)–N(1)	98.4(1)
O(4)–Cu(1)–N(1)	94.0(1)
O(3)–Cu(1)–N(1)	95.7(1)
O(1)–Cu(1)–N(1)	96.3(1)
O(2)–Cu(1)–Cu(1)*	84.24(8)
O(4)–Cu(1)–Cu(1)*	83.38(8)
O(3)–Cu(1)–Cu(1)*	83.97(8)
O(1)–Cu(1)–Cu(1)*	84.03(8)
Hydrogen bond	
N(2)–H(2)	0.95
H(2)···O(1)	1.99
N(2)···O(1)	2.912(4)
N(2)–H(2)–O(1)	162.7

Symmetry transformations used to generate equivalent atoms: *, $-x+2$, $-y+2$, $-z$.

The cobalt compound **3** changes colour from green (solid) to pink (solution). The solution spectrum may be explained in basis to an octahedral coordination. The absorption at 540 nm is assigned to the $^4T_{1g}(F) \rightarrow {}^4T_{1g}(P)$ transition. Of the three possible transitions for a d^7 high spin state: $^4T_{1g}(F) \rightarrow {}^4T_{2g}(F)$, $^4T_{1g}(F) \rightarrow {}^4A_{2g}(F)$ and $^4T_{1g}(F) \rightarrow {}^4T_{1g}(P)$, the first is of low energy and can be not observed and the second is a transition of two electrons (Scheme 2).

The diffuse reflectance spectrum corresponds to a d^7 high spin ion in a square-pyramidal (C_{4v}) environment [25]. The spectrum is similar to those described for the dimer [Co_2(μ-$O_2CPh)_4(quin)_2$] [10]. The transition $^4A_2 \rightarrow {}^4E$ ($^4T_{2g}$) can be of lower energy than the limit of the spectrophotometer (900 nm). The bands at 730, 585 and 440 nm are assigned to the transition to $^4B_1$, ^4E ($^4T_{1g}$) and $^4A_2$ ($^4T_{1g}$), respectively. The shoulders at 530 and 370 nm may be due to transitions to levels of the ^2G and ^2F free ion terms, respectively.

The reflectance spectrum of the nickel compound **4** is similar to those of [Ni_2(μ-$O_2CPh)_4(quin)_2$] [9]. Scheme 3 shows the splitting of the T(O_h) levels for a d^8 ion, in a square-pyramidal symmetry (C_{4v}). The transitions to $^3E[^3T_{2g}(F)]$, $^3B_2[^3T_{2g}(F)]$, and $^3A_2[^3T_{1g}(F)]$ are of low energy. The band at 690 nm is assigned to the $^3B_1 \rightarrow {}^3E[^3T_{1g}(F)]$ transition and the band at 410 nm to the non-resolved transitions to $^3A_2$ and ^3E levels of $^3T_{1g}(P)$. The solution spectrum is similar. The shoulder at 740 nm can be assigned to the spin forbidden $^3A_{2g} \rightarrow {}^1E_g$ transition, which frequently is observed near the $^3A_{2g} \rightarrow {}^3T_{1g}(F)$ transition when Dq/B is close to one. In this case, the assumption of 687 and 400 nm as the $^3A_{2g} \rightarrow {}^3T_{1g}(F)$ and $^3A_{2g} \rightarrow {}^3T_{1g}(P)$ transitions, respectively, allows to estimate the values $Dq = 830$ cm^{-1} and $B = 850$ cm^{-1} ($Dq/B = 0.98$). The absorption at 300 nm is assigned to charge transfer between metal and acetates.

For the zinc compound **5** only the ligand band and the charge transfer between metal and acetates are observed.

3.4. Magnetic results

Compounds of Cu(I), (**1**), and Zn(II), (**5**), are diamagnetic. Other three compounds **2**, **3** and **4** are antiferromagnetic.

The plots of $\chi_M T$ versus temperature (T) for compound **2** are shown in Fig. 3. The data, between 14 and 300 K, were fitted to the Bleaney–Bowers equation for a dimer with $S_1 = S_2 = 1/2$, modified by the inclusion of the fraction of monomeric impurity [26]:

$$\chi_M = [Ce^x(1-\rho)/(1+3e^x)] + C\rho/4 + N\alpha$$

where $C = Ng^2\beta^2/kT$, $x = 2J/kT$, ρ is the fraction of monomeric impurity and $N\alpha$ is the temperature independent paramagnetism (TIP). The results of the best fit for $g = 2.16$ (EPR result) and $N\alpha = 60 \times 10^{-6}$ cm^3 mol^{-1} are collected in Table 5. The $2J$ value, indicating a significant antiferromagnetic intradimer interaction, is similar to the values found in other adducts of copper acetate [27,28].

For Co(II) (**3**) and Ni(II) (**4**) complexes, a strong antiferromagnetic effect is observed. The magnetic moment decreases with decreasing temperature, from 3.03 (287 K) to 0.75 MB (4 K) for **3** and from 2.16 (293 K) to 1.24 MB (14 K) for **4**. This effect is still stronger than the found in other dimeric carboxylate complexes

Table 4
Electronic spectral data

Compound	λ_{max} (nm), in dimethylformamide	ε_{max} (l mol^{-1} cm^{-1})	λ (nm), diffuse reflectance
PhNHpy	274	25 900	360–190
2	700	193	725
	360	810	380
	300	10 030	310–190
	275	26 600	
3	540	39	730
	310	(sh)	585
	275	24 000	530(sh)
			440
			370(sh)
			360–190
			274
4	740	(sh)	690
	687	50	410
	400	230	310–190
	310	9440	
	274	24 000	
5	310	8000	380–190
	272	19 860	

sh, shoulder.

of Co(II) and Ni(II) [9,10,29]. These results are interpreted in basis to a dimeric structure, with an intramolecular interaction between the cations through the bridging acetate groups. The plots of $\chi_M T$ versus T (Fig. 4) have been fitted using the application of the Van Vleck equation to each case [30]. These are, with $C = Ng^2\beta^2/kT$, $x = 2J/kT$ and ρ = fraction of monomeric impurity, for cobalt(II) dimer ($S_1 = S_2 = 3/2$):

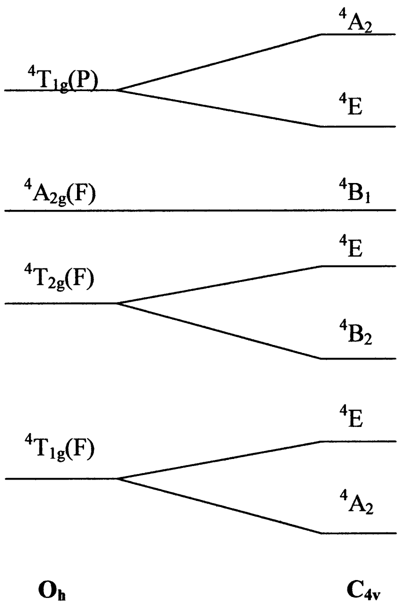
$$\chi_M = C[e^x + 5e^{3x} + 14e^{6x}](1-\rho)/[1 + 3e^x + 5e^{3x} + 7e^{6x}] + 5C\rho/4 + N\alpha$$

for nickel(II) dimer ($S_1 = S_2 = 1$):

$$\chi_M = C[e^x + 5e^{3x}](1-\rho)/[1 + 3e^x + 5e^{3x}] + 2C\rho/3 + N\alpha$$

The results of these fittings in the range 50–300 K, with $N\alpha = 60 \times 10^{-6}$ and 100×10^{-6}, for **3** and **4**, respectively, are summarized in Table 5.

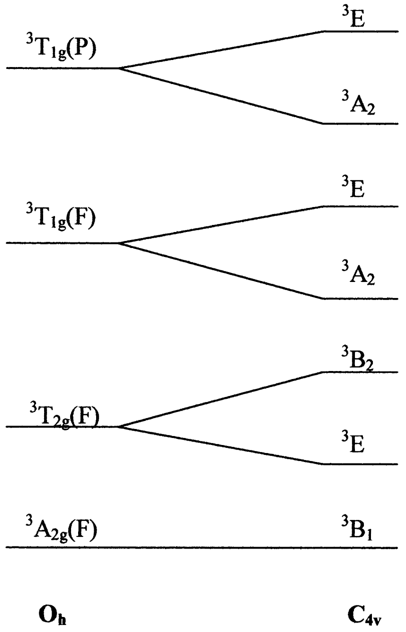
The magnetic behaviour below 50 K may be complicated by zero field splitting effects, especially in nickel compound, and other possible intermolecular interactions. The lack of knowledge of the crystal structure prevents us to make a more accurate interpretation. The conjunction of electronic spectra and magnetic results lets suppose a dimeric structure for the compounds **3** and **4**, $[M_2(\mu\text{-OAc})_4(PhNHpy)_2]$, similar to one of Cu(II) compound.



Scheme 2. Level splitting for d^7, high spin configuration, in C_{4v} symmetry.

3.5. EPR spectra

The powder EPR spectra of **2** in Q band, at room temperature, shows the typical signals of the triplet state ($S = 1$) for $D \neq 0$ and $E \approx 0$ (Fig. 5). The spectra were interpreted according to the Wasserman, Snyder and Yager equations [31,32], based on the Hamiltonian



Scheme 3. Level splitting for d^8 configuration in C_{4v} symmetry.

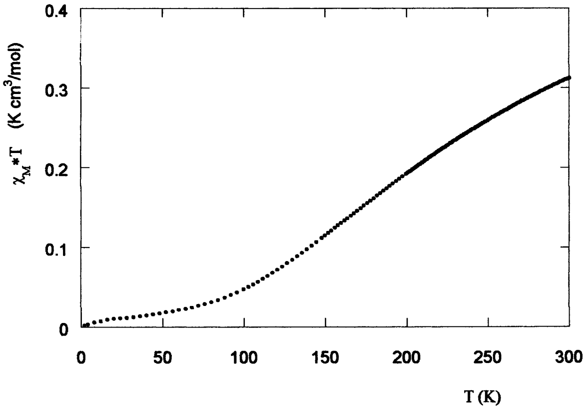


Fig. 3. Plot of χT versus T for **2**.

Table 5
Magnetic results

Compound	g	$2J$ (cm^{-1})	ρ	R[a]
2	2.12	-286[b]	0.0083	7.85×10^{-5}
3	4.27	-324[c]	0.020	2.46×10^{-4}
4	2.78	-382[d]	0.119	4.45×10^{-4}

[a] $R = \Sigma(\chi T_{\text{iexp}} - \chi T_{\text{ical}})^2 / \Sigma(\chi T_{\text{iexp}})^2$.

[b] Calculated from $\chi_M = [C e^x (1-\rho)/(1+3e^x)] + C\rho/4 + N\alpha$.

[c] Calculated from $\chi_M = C[e^x + 5e^{3x} + 14e^{6x}]\ (1-\rho)/[1+3e^x+5e^{3x}+7e^{6x}] + 5C\rho/4 + N\alpha$.

[d] Calculated from $\chi_M = C[e^x + 5e^{3x}]\ (1-\rho)/[1+3e^x+5e^{3x}] + 2C\rho/3 + N\alpha$.

$\mathscr{H} = gHS\beta + D[S_z^2 - 2/3] + E[S_x^2 - S_y^2]$, with $D \neq 0$ y $E = 0$. For $\Delta M = \pm 1$:

$$H_{\parallel} = (g_e/g_{\parallel})(H_o - D')$$

$$H_{\perp 1} = (g_e/g_{\perp})[H_o(H_o - D')]^{1/2}$$

$$H_{\perp 2} = (g_e/g_{\perp})[H_o(H_o + D')]^{1/2}$$

For $\Delta M = \pm 2$:

$$H_{\text{min}} = (g_e/g_{\text{min}})[(H_o^2/4) - (D'^2/3)]^{1/2}$$
$$H_{\text{dq}} = (g_e/g_{\text{av}})[H_o^2 - D'^2/3]^{1/2}$$

$$H_o = hv/g_e\beta;\ D' = D/g_e\beta$$

From the experimental values: $H_{\text{min}} = 4896$; $H_{\parallel} = 7262$; $H_{\perp 1} = 9755$; $H_{\perp 2} = 13\,317$ and $H_{\text{dq}} = 11\,035$ G, the following parameters have been calculated: $g_{\parallel} = 2.33$; $g_{\perp} = 2.07$; $g_{\text{av}} = 2.16$ and $D = 0.33$ cm^{-1}. These results agree with the results found for analogue compounds [23,28].

4. Supplementary material

Crystallographic data for the structural analysis have been deposited with the Cambridge Crystallographic Data Centre, CCDC No. 167019 for compound **2**. Copies of this information may be obtained free of charge from The Director, CCDC, 12 Union Road,

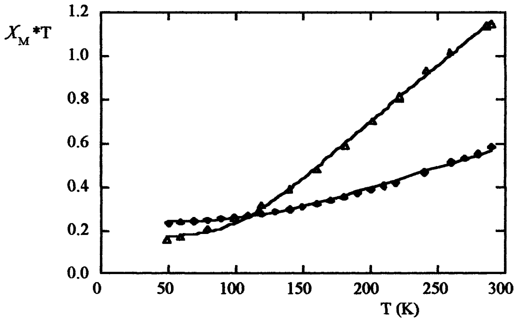


Fig. 4. Temperature dependence of χT for **3** (△) and **4** (◆).

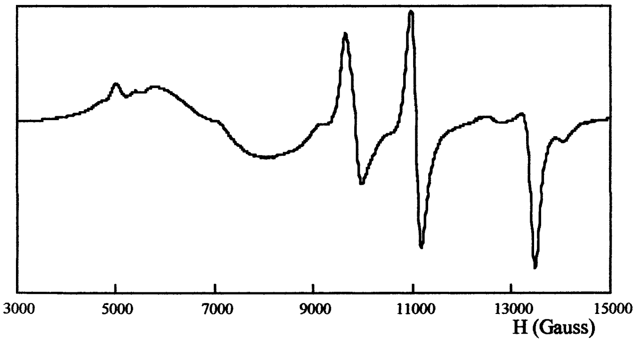


Fig. 5. EPR Q band spectrum of powdered $[Cu_2(\mu\text{-}OAc)_4(PhNHpy)_2]$ (**2**), at room temperature.

Cambridge, CB2 1EZ, UK (fax: +44-1223-336033; e-mail: deposit@ccdc.cam.ac.uk or www: http://www.ccdc.cam.ac.uk).

Acknowledgements

This work was supported by the 'Diputación Foral de Gipuzkoa'.

References

[1] P. De Meester, S.R. Fletcher, A.C. Skapski, J. Chem. Soc., Dalton Trans. (1973) 2575.
[2] R.L. Carlin, Magnetochemistry, Springer, Berlin Heidelberg, 1986.
[3] J. Catterick, P. Thornton, Adv. Inorg. Chem. Radiochem. 20 (1977) 291.
[4] R.J. Doedens, Progr. Inorg. Chem. 21 (1976) 209.
[5] V.M. Rao, D.N. Sathyanarayana, H. Manohar, J. Chem. Soc., Dalton Trans. (1983) 2167.
[6] M. Nakagawa, Y. Inomata, F.S. Howell, Inorg. Chim. Acta 295 (1999) 121.
[7] J.N. Van Niekerk, F.R.L. Schoening, Acta Crystallogr. 6 (1953) 609.
[8] J. Catterick, M.B. Hursthouse, P. Thornton, A.J. Welh, J. Chem. Soc., Dalton Trans. (1977) 223.
[9] A. Bencini, C. Benelli, D. Gatteschi, C. Zanchini, J. Am. Chem. Soc. 102 (1980) 5820.
[10] J. Catterick, P. Thornton, J. Chem. Soc., Dalton Trans. (1976) 1634.
[11] J.N. Van Niekerk, F.R.L. Schoening, Acta Crystallogr. 6 (1953) 720.
[12] A.R. Chakravarty, F.A. Cotton, Inorg. Chim. Acta 105 (1985) 19.
[13] D. Barr, W. Clegg, R.E. Mulvey, R. Snaith, J. Chem. Soc., Chem. Commun. (1984) 469.
[14] J.M. Seco, U. Amador, M.J. González Garmendia, Polyhedron 18 (1999) 3605.
[15] J.M. Seco, U. Amador, M.J. González Garmendia, Inorg. Chim. Acta 303 (2000) 256.
[16] D.A. Tocher, J.H. Tocher, Polyhedron 5 (1986) 1615.
[17] R.W. Brookes, R.L. Martin, Aust. J. Chem. 27 (1974) 1569.
[18] G.M. Sheldrick, 'SHELXL-97. A Program for Refinement of Crystal Structure', University of Göttingen. 1977.
[19] I.D. Brown, J.D. Dunitz, Acta Crystallogr. 14 (1961) 480.
[20] F.A. Cotton, X. Feng, M. Matusz, R. Poli, J. Am. Chem. Soc. 110 (1988) 7077.
[21] (a) F.A. Cotton, X. Feng, D.J. Timmons, Inorg. Chem. 37 (1998) 4066;
(b) H. Aghabozorg, H. Hosseini-Monfarred, Iran. J. Chem. Chem. Eng. 14 (1995) 6.
[22] G. Smith, C.H. Kennard, K.A. Byriel, Polyhedron 8 (1991) 873.
[23] F. Sapiña, M. Burgos, E. Escriva, J.V. Folgado, D. Beltrán, P. Gómez Romero, Inorg. Chim. Acta 216 (1994) 185.
[24] B.J. Edmonson, A.B.P. Lever, Inorg. Chem. 4 (1965) 1608.
[25] A.B.P. Lever, Inorganic Electronic Spectroscopy, 2nd ed., Elsevier, 1984.
[26] M. Nakashima, M. Mikuriya, Y. Muto, Bull. Chem. Soc. Jpn. 58 (1985) 968.
[27] M. Melník, Coord. Chem. Rev. 42 (1982) 259.
[28] J.S. Valentine, A.J. Silverstein, Z.G. Soos, J. Am. Chem. Soc. 96 (1974) 97.
[29] J. Catterick, P. Thornton, J. Chem. Soc., Dalton Trans. (1975) 233.
[30] C.J. O'Connor, Progr. Inorg. Chem. 29 (1982) 203.
[31] E. Wasserman, L.C. Snyder, W.A. Yager, J. Chem. Phys. 41 (1964) 1763.
[32] A. Bencini, D. Gatteschi, EPR of Exchange Coupled Systems, Springer, Berlin, 1990.