

Inorganica Chimica Acta 260 (1997) 1-9

Inorganica Chimica Acta

# Metal complexes with disubstituted oxamidic ligands

U. Casellato, P. Guerriero, S. Tamburini, P.A. Vigato \*

Istituto di Chimica e Tecnologie Inorganiche e dei Materiali Avanzati, CNR, C.so Stati Uniti 4, 35127 Padua, Italy

Received 1 February 1996; accepted 30 September 1996

#### Abstract

Three oxamidic ligands have been prepared by reaction of oxalyldichloride with the appropriate amine  $H_2NC_6H_4P(C_6H_5)_2$  ( $H_2A$ ),  $H_2NC_2H_4(NC_5H_4)$  (H<sub>2</sub>B) and  $H_2NC_2H_4SC_6H_5$  (H<sub>2</sub>C). They have been characterized by elemental analyses, IR, NMR, mass spectrometry and for H<sub>2</sub>B by X-ray diffractometry. The crystals, grown from a tetrahydrofuran/diethylether solution, are monoclinic, space group  $P2_1/c$ , cell dimensions a = 9.503(4), b = 6.278(4), c = 13.083(5) Å and  $\beta = 100.24(4)^\circ$  with Z = 2. The asymmetric unit is half of the ligand molecule which shows an inversion centre between the C-C bond of the oxamidic group. The molecule is elongated in a three steps configuration. The reaction of  $H_2A$  with trans-Pd( $C_6H_5CN$ )<sub>2</sub>(Cl)<sub>2</sub> forms the white mononuclear cis-Pd(A) and the yellow homodinuclear trans-Pd<sub>2</sub>(A)(Cl)<sub>2</sub> complexes as confirmed by scanning electron microscopy (SEM) and EDX analyses and by an X-ray structure of  $Pd_2(A)(Cl)_2$ . The yellow crystals, grown from alcoholic solution, are monoclinic, space group  $P2_1/c$ , cell dimensions a = 10.335(5), b = 10.246(5), c = 16.480(6) Å and  $\beta = 100.81(5)^{\circ}$  with Z = 2; as for H<sub>2</sub>B crystals, the asymmetric unit is half of the whole molecule. A distorted square planar coordination around each metal ion is reached by the coordination of a phosphorus, an oxygen and a nitrogen atom of the ligand and a chlorine atom.  $H_2B$  forms the homodinuclear nickel(II) and copper(II) complexes M(B)(X)<sub>2</sub> (X=Cl<sup>-</sup>, CH<sub>3</sub>COO<sup>-</sup>,  $ClO_4^-$ ). Crystals of the dinuclear copper(II) complex  $Cu_2(B)(Cl)_2(dmso)_2$ , grown from dimethylsulphoxide, are triclinic, space group  $P\overline{1}$ , cell dimensions a = 8.352(5), b = 8.361(5), c = 9.959(4) Å,  $\alpha = 83.39(4)$   $\beta = 85.49(3)$ ,  $\gamma = 75.38(5)^{\circ}$  with Z=1. Again the dinuclear entity shows a inversion centre between the two C-C bonds of the oxamide ligand. Each copper(II) ion has a distorted square pyramidal environment formed by two nitrogen atom and an oxygen atom of half oxamidic ligand, a chlorine atom and the oxygen atom of a dimethylsulphoxide molecule; the copper-copper distance is 5.28 Å. An antiferromagnetic interaction was observed for the dinuclear copper(II) complexes. H<sub>2</sub>C does not form complexes when reacted with transition metal ions.

Keywords: Crystal structures; Transition metal complexes; Palladium complexes; Oxamidic acid complexes

## 1. Introduction

Many studies have been devoted to the design and synthesis of di- and poly-nucleating macrocyclic or macroacyclic ligands and related homo and/or heteronuclear complexes and to the interaction between metal ions connected by appropriate bridges [1–4]. These systems offer the possibility of a knowledge of the magnetic pathway between paramagnetic centres and more generally of the fundamental factors governing physico-chemical properties of the complexes containing d- and/or f-metal ions [5]. An appropriate design of these compounds makes them suitable building blocks to obtain new materials. Moreover spin exchange, charge transfer, etc., between metal ions in polymetallic systems are of paramount relevance experimentally and theoretically in the study of biological metallic sites and/or their chemical models [6–10]. *N,N'*-disubstituted oxamides are versatile ligands for the design and preparation of polynuclear systems [11–17]. Their  $cis \rightarrow trans$  isomerization favours the formation of well defined mononuclear, homo or heteropolynuclear complexes. The ligands in the *cis*-configuration easy produce mononuclear complexes, which may be used as 'ligands' for subsequent heteronuclear complexation. On the contrary the *trans*-configuration leads to the formation of homodinuclear complexes, which may give rise to polynuclear species by intermolecular aggregation [18–20].

It was found that in these polynuclear complexes the oxamidic group is an excellent bridging mediator of magnetic exchange between neighbouring paramagnetic centres, the type and magnitude of coupling depending on the metal ion used and its coordination environment [11–32]. Thus the aminoamides N,N'-bis(3-aminopropyl)oxamide or N,N'bis(2-amino-2,2-dimethylethyl)oxamide form, under suitable experimental conditions, mononuclear or homodinuclear copper(II) complexes and heterodinuclear or -trinuclear

<sup>\*</sup> Corresponding author.

<sup>0020-1693/97/\$17.00 © 1997</sup> Elsevier Science S.A. All rights reserved  $\it PII\,S\,00\,20-1\,693\,(\,96\,)\,0\,5\,5\,20$  - X

complexes containing d,d or d,f metal ions [11,12,14– 18,24,26]. Moreover an oligomerization or polymerization of the dinuclear or trinuclear entities through the oxygen atoms of the oxamidic ligands or the donor atoms of the counter anions (i.e. Cl<sup>-</sup>, CH<sub>3</sub>COO<sup>-</sup>, NCO<sup>-</sup>, etc.) may occur giving rise to zigzagging chains [19,21,26]. The Xray structural determinations of these complexes and an appropriate study of their magnetic properties have given essential information for a rationalization of the magnetic coupling of paramagnetic species through the oxamide bridge, allowing correct magneto-structural correlations also in polymeric species.

In the present paper we report the preparation and properties of the functionalized oxamide compounds  $H_2A\cdots H_2C$ obtained by reaction of oxalyldichloride and the appropriate amine  $H_2N-R$  [ $R = C_6H_4P(C_6H_5)_2$ ,  $CH_2CH_2(C_5H_4N)$ ,  $CH_2CH_2S(C_6H_5)$ ] in the presence of base, and related complexes containing palladium(II), platinum(II), copper(II) or nickel(II) together with the X-ray structure of  $H_2B$  and of the dinuclear complexes  $Pd_2(A)(Cl)_2$  and  $Cu_2(B)(Cl)_2$ -(dmso)<sub>2</sub>.



During these investigations it was observed that it was almost impossible to form heterodinuclear complexes: all the attempts to synthesize these compounds, under different experimental conditions, led to the formation of homodinuclear complexes.

## 2. Experimental

#### 2.1. Materials

Oxalyldichloride, 2-(2-aminoethyl)pyridine, 2-aminoethyl, phenyl-sulphide, triethylamine, the salts and the solvents were commercial products used without further purification, while tetrahydrofuran was anhydrified and purified following literature methods [33]. Also 2-(diphenylphosphino)-aniline, *trans*-Pd(C<sub>6</sub>H<sub>5</sub>CN)<sub>2</sub>(Cl)<sub>2</sub> and *trans*-Pt-(CH<sub>3</sub>CN<sub>2</sub>)(Cl)<sub>2</sub> were prepared according to literature [34].

Pyridine-2,6-dialdehyde was prepared by oxidation at room temperature of pyridine-2,6-dimethanol (Aldrich) with activated  $MnO_2$  in CHCl<sub>3</sub>. The CHCl<sub>3</sub> solution was stirred for 4 days, then evaporated to dryness and the crude product was purified by silica gel chromatography using CH<sub>2</sub>Cl<sub>2</sub> as eluant [35].

The elemental analyses of the prepared ligands and related complexes are reported in Table 1.

#### 2.1.1. Preparation of $H_2A$ , $H_2B$ and $H_2C$

For the preparation of the three ligands, the following experimental procedure was employed [36]: oxalyldichloride (10 mmol) in anhydrous tetrahydrofuran (50 mmol) was added dropwise and under nitrogen to an anhydrous tetrahydrofuran solution (100 ml) of the appropriate amine (20 mmol) and triethylamine (2 mmol). The resulting suspension was stirred at room temperature and under a nitrogen flux for 24 h. The white precipitate was filtered and the tetrahydrofuran solution was partially evaporated under reduced pressure. By the addition of diethylether to this reduced solution obtained, a pale yellow or white precipitate was obtained. It was filtered, washed with diethylether and dried in vacuo.

The melting points of the prepared compounds are  $H_2A$  at 215–216°C,  $H_2B$  at 174–175°C and  $H_2C$  at 199–200°C.  $H_2A$  and  $H_2B$  are soluble in all the common organic solvents.

## 2.1.2. Preparation of cis-Pd(A) and trans- $Pd_2(A)(Cl)_2$

To a CHCl<sub>3</sub> solution (50 ml) of H<sub>2</sub>A (0.5 mmol, 304 mg), *trans*-Pd(C<sub>6</sub>H<sub>5</sub>CN)<sub>2</sub>(Cl)<sub>2</sub> (0.5 mmol, 191.5 mg) in MeOH (50 ml) and triethylamine (1 mmol) were added at room temperature. The solution was refluxed for 24 h. The yellow precipitate formed was filtered. It contains *cis*-Pd(A) and *trans*-Pd<sub>2</sub>(A)(Cl)<sub>2</sub> which were separated by extraction in a soxhlet with tetrahydrofuran. *cis*-Pd(A) is extracted and obtained as white needles from the tetrahydrofuran solution, while the residue is the *trans*-Pd<sub>2</sub>(A)(Cl)<sub>2</sub> in a pure yellow form. The yellow *trans*-Pd(A)(Cl)<sub>2</sub> can be recrystallized form an alcoholic solution and gives rise to yellow rhombi suitable for an X-ray investigation.

2.1.3. Preparation of  $M_2(B)(H_2B)(X)_2 \cdot nS$  ( $M = Ni, X = Cl^-, CH_3COO^-, M = Cu, X = ClO_4^-, n = 0-5, S = H_2O, EtOH$ )

To a boiling ethanolic solution (50 ml) of  $H_2B$  (0.5 mmol), the appropriate metal(II) salt (0.5 mmol) dissolved in the minimum volume of  $H_2O$  (5 ml) and triethylamine (1 mmol) were added. The resulting solution was refluxed for 3 h, then evaporated to dryness. The residue was dissolved in ethanol and precipitated with diethyl ether. The precipitate was collected by filtration, washed twice with a 1:1 ethanol/diethylether solution and dried in vacuo.

2.1.4. Preparation of  $M_2(B)(X)_2$  ( $M = Cu^{2+}$ ,  $Ni^{2+}$ ;  $X = Cl^-$ ,  $CH_3COO^-$ )

To a boiling ethanolic solution (50 ml) of  $H_2B$  (0.5 mmol), the appropriate metal salt (0.5 mmol) dissolved in the minimum volume of  $H_2O$  (5 ml) and triethylamine (1 mmol) were added. The resulting solution was refluxed for 3 h, then evaporated to dryness. The residue was treated with ethanol, collected by filtration, washed with ethanol and dried in vacuo.

## 2.2. X-ray crystallography

The cell parameters and intensity data were collected on a Philips PW1100 (FEBO System) automatic diffractometer

Table 1
Elemental analyses of the prepared ligands and related complexes

Complex	Found (%)			Calc. (%)	Calc. (%)	
	С	Н	N	С	Н	Ν
H <sub>2</sub> A	74.99	4.60	4.97	75.00	4.33	5.16
H <sub>2</sub> B	64.42	18.78	6.08	63.87	18.80	6.43
H <sub>2</sub> C	59.97	7.77	5.59	59.99	7.85	5.79
$[Pd(A)] \cdot 2(H_2O)$	61.28	3.76	3.17	60.94	4.31	3.74
$Pd_2(A)(Cl)_2$	50.85	2.95	3.00	51.27	3.17	3.15
$Ni_2(B)(H_2B)(Cl)_2 \cdot 5(H_2O) \cdot EtOH$	43.92	5.00	11.64	44.43	5.48	12.19
$Ni_{2}(B)(H_{2}B)](Ac)_{2} \cdot 4H_{2}O$	48.17	4.94	12.44	47.93	5.36	12.42
$Cu_2(B)(H_2B)(ClO_4)_2(EtOH)_2$	43.49	4.49	11.15	42.78	4.39	11.09
$Cu_2(B)(Cl)_2$	39.04	3.48	10.86	38.88	3.26	11.33
$Cu_2(B)(Ac)_2$	44.00	4.09	9.84	44.36	4.10	10.35
$Cu_2(B)(ClO_4)_2 \cdot 4H_2O$	27.10	3.05	8.20	27.68	3.48	8.07
$Ni_2(B)(Ac)_2$	45.00	3.95	11.05	45.17	4.17	10.53
$Ni_2(B)(Cl)_2$	39.25	2.95	11.40	39.65	3.33	11.65

using Mo K $\alpha$  radiation ( $\lambda = 0.71069$  Å) and  $\omega - 2\theta$  scan method. Owing to its instability in air, the copper complex was sealed into a quartz capillary with its mother liquor. No appreciable decomposition was observed during data collections.

All intensity data were corrected for Lorentz and polarization effects. Because of the relatively high absorption coefficients of the palladium and copper complexes, absorption corrections were applied based on  $\psi$ -scans of three strong reflections [37].

The three structures were solved by direct methods/Patterson and Fourier methods and subsequent refinement by full-matrix least-squares; a unit weighting scheme was applied.

In all three data sets, reflections with  $I \ge 3\sigma(I)$  were considered observed and used in the structural analyses. Anisotropy was introduced for all non-hydrogen atoms.

Hydrogen bonded to carbon atoms were introduced in calculated positions with fixed C–H distances and isotropic temperature factors (C–H = 1.08 Å,  $U_{iso}$  = 0.08 Å<sup>2</sup>).

Crystal and intensity data for the compounds are reported in Table 2; atomic positional parameters with estimated standard deviations are listed in Tables 3–5; selected bond distances and angles in Tables 6 and 7 Table 8.

The thermal and hydrogen atom positional parameters and observed/calculated structural factors have been deposited as Supplementary Material.

All calculations were carried out on a DIGITAL ALPHA-AXP 300 computer and using SHELX-76 and SHELX-86 [38] programs.

### 2.3. Physico-chemical measurements

IR spectra were recorded as KBr pellets on a Mattson FTIR 3000 spectrometer.

<sup>1</sup>H and <sup>13</sup>C NMR spectra were recorded at 200.132 MHz on a Bruker AC200 spectrometer equipped with an Aspect 3000 computer at room temperature. Some of the signals were assigned by the spin decoupling technique. All the samples examined were dissolved in hot  $dmso-d_6$  or  $CDCl_3$  used also as internal references.

The homogeneity of the heteropolynuclear samples was checked by using a Philips XL40 model scanning electron microscopy equipped with an EDAX PV99 X-ray energy dispersive spectrometer. Metal ratios were determined by energy dispersive X-ray spectrometry (EDX) [39].

The solvent content (H<sub>2</sub>O or MeOH) was evaluated by thermal analysis curves using a Netzsch STA 429 thermoanalytical equipment. The tests were performed in a nitrogen atmosphere (flux rate 250 ml min<sup>-1</sup>; heating rate  $5^{\circ}$ C min<sup>-1</sup>) and in air under the same conditions. Neutral alumina (Carlo Erba product) was used as reference material.

All mass spectrometric measurements were performed on a VG ZAB 2F instrument (VG analytical Ltd.) operating in electron impact (EI) (70 eV, 200 mA, ion source temperature 200°C) and fast atom bombardment (FAB) (8 keV Xe atom bombarding a thioglicerol/acetic solution of the sample) conditions [40,41].

Magnetic susceptibilities were determined by the Faraday method at room temperature, the apparatus (Oxford Instruments) being calibrated with  $HgCo(NCS)_4$  [42]. Diamagnetic corrections were performed [43].

## 3. Results and discussion

The phosphino-oxamidic ligand H<sub>2</sub>A was prepared by reaction of oxalyldichloride and 2-(diphenyl-phosphino)aniline in anhydrous tetrahydrofuran in the presence of triethylamine. It is a white solid, very stable in air; as expected the phosphinic group is not oxidized to the corresponding phosphine oxide. It is very soluble in tetrahydrofuran and CHCl<sub>3</sub>, but shows a low solubility in other organic solvents (i.e. MeOH, EtOH, CH<sub>3</sub>CN, Et<sub>2</sub>O). The IR spectrum shows a band at 3325 cm<sup>-1</sup> due to  $\nu_{N-H}$  and a strong absorption at 1696 cm<sup>-1</sup> attributed to  $\nu_{C=O}$  of the amidic groups. The <sup>1</sup>H

Table 2
Crystal and intensity data for $H_2B$ , $Pd_2(A)(Cl)_2$ , and $Cu_2(B)(Cl)_2(dmso)_2$

Compound	H <sub>2</sub> B	$Pd_2(A)(Cl)_2$	$Cu_2(B)(Cl)_2(dmso)_2$
Formula	$C_{16}H_{18}N_4O_2$	$C_{38}H_{28}N_2O_2Cl_2P_2Pd_2$	$C_{20}H_{28}N_4O_4S_2Cl_2Cu_2$
Formula weight	299.8	892.3	650.6
Colour and habit	colourless, irregular blocks	vellow prisms	green prisms
Crystal size (mm)	$0.32 \times 0.24 \times 0.18$	$0.25 \times 0.20 \times 0.33$	$0.19 \times 0.38 \times 0.23$
Crystal system	monoclinic	monoclinic	triclinic
Space group	$P2_1/c$ (No. 14)	$P2_1/c$ (No. 14)	<i>P</i> 1 (No. 2)
Cell parameters	• • •	• • •	· · · ·
a (Å)	9.503(4)	10.335(5)	8.352(5)
$b(\dot{A})$	6.278(4)	10.246(5)	8.361(5)
c (Å)	13.083(5)	16.480(6)	9.959(4)
$\alpha$ (°)			83.39(4)
$\beta$ (°)	100.24(4)	100.81(5)	85.49(3)
$\gamma$ (°)			73.38(5)
Cell volume ( $Å^3$ )	768.1	1714	667.6
Ζ	2 ª	2 <sup>a</sup>	1 <sup>a</sup>
Calc. density $(g cm^{-3})$	1.29	1.72	1.62
T(K)	295	295	295
<i>F</i> (000) (elec.)	316	884	332
Absorption $\mu$ (cm <sup>-1</sup> ) (Mo K $\alpha$ )	0.52	12.11	19.89
Data collected ( $2\theta$ limits)	1032 (6–61°)	2030 (6.4–59.8°)	2147 (5.0-50°)
Unique data	973 <sup>b</sup>	1959 <sup>ь</sup>	1971
Data with $I > 3\sigma(I)$	937	1924	1901
Transmission coeff.		0.787-0.988	0.884-1.00
Number of param. (observ. per param.)	127 (7.4)	181 (10.6)	172 (11.1)
R <sup>°</sup>	0.036	0.028	0.025
GOF	0.34	1.58	0.55
Highest shift/e.s.d.	0.865	0.001	0.004
Highest map residual (e $Å^{-3}$ )	0.16	0.382	0.372

<sup>a</sup> The asymmetric unit is half of the whole molecule.

<sup>b</sup> Owing to the poor quality of the crystals, a low number of reflections has been collected.

 $^{c}R = \sum (|F_{o}| - |F_{c}|) / \sum (F_{o}).$ 

Table 3	
Fractional coordinates with equivalent	isotropic thermal parameters for H2B

Atom	x	у	z	$U_{\rm eq}^{\ a}  ({\rm \AA}^2)$
N(1)	0.7861(2)	0.7544(3)	0.7295(1)	0.0523(6)
C(1)	0.6857(3)	0.8747(4)	0.7615(2)	0.0667(9)
C(2)	0.5533(3)	0.9116(4)	0.7035(2)	0.066(1)
C(3)	0.5217(2)	0.8251(4)	0.6068(2)	0.0639(8)
C(4)	0.6238(2)	0.7054(4)	0.5715(2)	0.0559(7)
C(5)	0.7550(2)	0.6704(3)	0.6346(1)	0.0415(6)
C(6)	0.8669(2)	0.5319(4)	0.6008(2)	0.0527(8)
C(7)	0.8560(2)	0.3017(3)	0.6370(2)	0.0480(7)
C(8)	0.9372(2)	0.0689(3)	0.5103(1)	0.0446(6)
N(2)	0.9605(2)	0.1634(3)	0.6026(1)	0.0469(5)
O(1)	0.8272(1)	0.0849(3)	0.4456(1)	0.0647(6)

<sup>a</sup>  $U_{eq}$  is defined as one third of the trace of the orthogonalized  $U_{ij}$  tensor.

NMR spectrum in  $\text{CDCl}_3$  shows a peak at 10.06 ppm due to the amidic NH protons while the peaks at 8.02, 7.07, 6.86 and 6.73 ppm are due to the aromatic protons. No signals due to the presence of phosphine-oxide groups are present in the IR and NMR spectra.

H<sub>2</sub>A reacts with *trans*-Pd(C<sub>6</sub>H<sub>5</sub>)<sub>2</sub>(Cl)<sub>2</sub> in CHCl<sub>3</sub> and in the presence of base (NEt<sub>3</sub>), giving rise to the mononuclear *cis*-Pd(A) and the homodinuclear, *trans*-Pd(A)(Cl)<sub>2</sub> according to the Scheme 1.

SEM investigations show white needles and yellow rhombi for the palladium(II) complexes, which are attributable to the *cis* and *trans* form, respectively, on the basis of EDX analyses. A careful investigation, carried out on both samples by means of the microprobe, evidences a Pd:P ratio of 1:2 in the white needles and a Pd:P:Cl ratio of 1:1:1 in the yellow rhombi, confirming the presence of both compounds.

A subsequent soxhlet extraction of the mixture of *cis*- and *trans*-palladium(II) complexes by tetrahydrofuran, allows a separation of the more soluble *cis* from the *trans* complex. The two compounds show very similar IR spectra. In particular a strong band at 1647 cm<sup>-1</sup>, due to the  $\nu_{C=0}$  of the amidic group, is clearly detectable; *trans*-Pd<sub>2</sub>(A)(Cl)<sub>2</sub> shows an additional IR band at 322 cm<sup>-1</sup> due to  $\nu_{Pd-Cl}$ .

By recrystallization of *trans*-Pd<sub>2</sub>(A)(Cl)<sub>2</sub> from an alcoholic solution, yellow crystals suitable for an X-ray investigation were obtained. A perspective view of the complex with atom labelling is shown in Fig. 1. Selected bond lengths and angles are given in Table 7. The asymmetric unit is formed by half a molecule of the complex which shows an inversion centre between the carbon atoms C(1)-C(1') of the oxamidic group. The centre of the molecule is almost planar, except for the benzene rings of the phosphine groups. Each palladium(II) atom is in a distorted square planar environment, being coordinated by a phosphorus, an oxygen and

Table 4 Fractional coordinates with equivalent isotropic thermal parameters for  $Pd_2(A)(Cl)_2$ 

Atom	x	у	z	$U_{\mathrm{eq}}^{\mathrm{a}}(\mathrm{\AA}^2)$
Pd(1)	0.19311(4)	0.10516(4)	0.11646(2)	0.0280(1)
Cl(1)	0.4150(1)	0.0861(2)	0.16042(9)	0.0462(5)
O(1)	0.1702(3)	-0.0371(4)	0.0214(2)	0.038(1)
C(1)	0.0524(5)	-0.0417(5)	-0.0159(3)	0.032(2)
N(1)	-0.0039(4)	0.1109(4)	0.0818(2)	0.030(1)
P(1)	0.1694(1)	0.2655(1)	0.19880(8)	0.0302(4)
C(3)	-0.2164(3)	0.1835(3)	0.1180(2)	0.040(2)
C(4)	-0.2801(3)	0.2534(3)	0.1716(2)	0.048(2)
C(5)	-0.2067(3)	0.3274(3)	0.2351(2)	0.053(2)
C(6)	-0.0698(3)	0.3314(3)	0.2450(2)	0.043(2)
C(7)	-0.0061(3)	0.2615(3)	0.1913(2)	0.033(2)
C(2)	-0.0794(3)	0.1875(3)	0.1278(2)	0.031(2)
C(9)	0.3451(3)	0.4540(3)	0.1665(2)	0.044(2)
C(10)	0.3799(3)	0.5714(3)	0.1334(2)	0.055(2)
C(11)	0.2822(3)	0.6549(3)	0.0928(2)	0.064(3)
C(12)	0.1498(3)	0.6210(3)	0.0853(2)	0.064(3)
C(13)	0.1150(3)	0.5036(3)	0.1183(2)	0.051(2)
C(8)	0.2127(3)	0.4201(3)	0.1589(2)	0.031(2)
C(15)	0.2209(4)	0.1395(3)	0.3463(2)	0.058(2)
C(16)	0.2758(4)	0.1226(3)	0.4297(2)	0.069(3)
C(17)	0.3527(4)	0.2212(3)	0.4729(2)	0.059(3)
C(18)	0.3746(4)	0.3367(3)	0.4327(2)	0.059(2)
C(19)	0.3197(4)	0.3537(3)	0.3494(2)	0.051(2)
C(14)	0.2429(4)	0.2550(3)	0.3062(2)	0.035(2)

<sup>a</sup>  $U_{eq}$  is defined as one third of the trace of the orthogonalized  $U_{ij}$  tensor.

Table 5

Fractional coordinates with equivalent isotropic thermal parameters for  $\text{Cu}_2(B)(\text{Cl})_2(\text{dmso})_2$ 

Atom	x	у	Ζ	$U_{\rm eq} ^{\rm a} ({\rm \AA}^2)$
Cu(1)	0.22377(4)	0.29439(4)	0.15255(3)	0.0323(1)
Cl(1)	0.1893(1)	0.09950(8)	0.32323(7)	0.0463(2)
O(1)	-0.0199(2)	0.4021(2)	0.1645(2)	0.0363(7)
O(2)	0.2720(3)	0.5054(2)	0.2693(2)	0.0478(7)
N(1)	0.4715(3)	0.2049(2)	0.1301(2)	0.0343(8)
C(1)	0.5562(4)	0.1669(3)	0.2444(3)	0.044(1)
C(2)	0.7266(4)	0.1183(4)	0.2424(4)	0.051(1)
C(3)	0.8144(4)	0.1097(4)	0.1218(4)	0.052(1)
C(4)	0.7297(4)	0.1467(4)	0.0045(4)	0.050(1)
C(5)	0.5584(3)	0.1941(3)	0.0102(3)	0.0355(9)
C(6)	0.4653(3)	0.2337(3)	-0.1181(3)	0.0397(9)
C(7)	0.3477(3)	0.4070(3)	-0.1295(3)	0.038(1)
N(2)	0.2108(3)	0.4130(3)	-0.0296(2)	0.0330(7)
C(8)	0.0641(3)	0.5046(3)	-0.0565(2)	0.0304(9)
S(1)	0.1481(1)	0.54333(8)	0.38591(7)	0.0432(3)
C(9)	0.2453(5)	0.6295(5)	0.5040(4)	0.071(2)
C(10)	-0.0003(4)	0.7315(4)	0.3354(3)	0.056(1)

<sup>a</sup>  $U_{eq}$  is defined as one third of the trace of the orthogonalized  $U_{ii}$  tensor.

a nitrogen atom of the ligand, which behaves as a dinucleating hexadentate chelate. A chlorine atom fills the fourth coordination site. Thus the organic ligand forms with the central metal ion two five-membered rings with bond angles of  $81.0(2)^{\circ}$  for O(1)-Pd(1)-N(1) and  $85.9(1)^{\circ}$  for N(1)-Pd(1)-P(1). The bond distances related to the coordination are: Pd–Cl 2.280(1) Å, Pd–O 2.121(3) Å, Pd–N

Table 6 Selected bond distances (Å) and angles (°) for  $H_2B$ 

N(1)-C(1)	1.341(3)	N(1)-C(5)	1.333(2)
C(1)-C(2)	1.368(3)	C(2) - C(3)	1.361(4)
C(3) - C(4)	1.370(3)	C(4) - C(5)	1.385(3)
C(5)-C(6)	1.500(3)	C(6) - C(7)	1.530(3)
C(7)-N(2)	1.450(3)	C(8)–N(2)	1.328(3)
C(8)-O(1)	1.227(2)		
$N(1)\cdots N(2^a)$	3.012(2)		
C(1)-N(1)-C(5)	117.5(2)	N(1)-C(1)-C(2)	123.9(2)
C(1)-C(2)-C(3)	118.4(2)	C(2)-C(3)-C(4)	118.7(2)
C(3)-C(4)-C(5)	120.2(2)	N(1)-C(5)-C(4)	121.3(2)
C(4)-C(5)-C(6)	121.8(2)	N(1)-C(5)-C(6)	116.9(2)
C(5)-C(6)-C(7)	111.5(2)	C(6)-C(7)-N(2)	112.4(2)
N(2)-C(8)-	125.1(2)	C(7)-N(2)-C(8)	122.5(2)
O(1)			

<sup>a</sup> Symmetry code = 2 - x, 0.5 + y, 1.5 - z.

Table 7 Selected bond distances (Å) and angles (°) for  $Pd_2(A)(Cl)_2$ 

Pd(1)-Cl(1)	2.280(2)	Pd(1)-O(1)	2.121(4)
Pd(1) - N(1)	2.010(4)	Pd(1) - P(1)	2.173(2)
O(1) - C(1)	1.258(6)	N(1)-C(2)	1.422(5)
P(1)-C(7)	1.795(3)	P(1)-C(8)	1.803(4)
P(1)-C(14)	1.793(4)	C(3)–C(4)	1.395(5)
N(1)-Pd(1)-P(1)	85.9(1)	O(1)-Pd(1)-P(1)	166.1(1)
O(1) - Pd(1) - N(1)	81.0(2)	Cl(1)-Pd(1)-P(1)	95.20(8)
Cl(1)-Pd(1)-N(1)	176.2(1)	Cl(1)-Pd(1)-O(1)	98.2(1)
Pd(1)-O(1)-C(1)	110.5(3)	Pd(1)-N(1)-C(2)	119.5(3)
Pd(1)-P(1)-C(14)	119.7(1)	Pd(1)-P(1)-C(8)	111.8(1)
Pd(1)-P(1)-C(7)	99.8(1)	C(8)-P(1)-C(14)	108.9(2)
C(7) - P(1) - C(14)	107.6(2)	C(7) - P(1) - C(8)	108.1(2)
P(1)-C(7)-C(6)	122.4(3)	P(1)-C(7)-C(2)	117.6(3)
N(1)-C(2)-C(7)	115.1(3)	N(1)-C(2)-C(3)	124.6(3)
P(1)-C(8)-C(13)	120.5(3)	P(1)-C(8)-C(9)	119.5(3)
P(1)-C(14)-C(19)	123.8(3)	P(1)-C(14)-C(15)	116.2(3)

2.010(4) Å and Pd–P 2.173(1) Å. The metal ion lies approximately in the mean plane of the coordinating atoms O(1), P(1) and Cl(1) (0.003 Å above). The Pd...Pd distance is 5.44 Å; the other bond distances and angles are normal. There are no significant intermolecular interactions, thus the binuclear entities are isolated in the crystal packing.

Attempts to obtain heterodinuclear complexes, using *cis*-Pd(A) as 'ligand' and copper(II), nickel(II) or lanthanum(III) salts, failed: in each case the final compound recovered and characterized is the homodinuclear *trans*-Pd<sub>2</sub>-(A)(X)<sub>2</sub>.

By using an experimental procedure similar to that employed for  $H_2A$  we have prepared the ligands  $H_2B$  and  $H_2C$ , containing respectively pyridinic or thioether groups. Thus, by reaction of oxalyldichloride and 2-(2-aminoethyl)pyridine or 2-aminoethyl, phenylsulphide in anhydrous tetrahydrofuran and in the presence of NEt<sub>3</sub>, white solids of the two functionalized amides have been obtained in good yields.  $H_2B$  is very soluble in the common organic solvents and insoluble in diethylether while  $H_2C$  is soluble only in

Table 8 Selected bond distances (Å) and angles (°) for  $Cu_2(B)(Cl)_2(dmso)_2$ 

Cu(1)–Cl(1)	2.269(1)	Cu(1)–O(1)	2.007(2)
Cu(1)–N(2)	1.962(2)	Cu(1) - N(1)	2.019(2)
N(1)-C(1)	1.351(4)	N(1)-C(5)	1.348(3)
C(1)-C(2)	1.377(5)	C(2) - C(3)	1.357(5)
C(3)–C(4)	1.377(5)	C(4) - C(5)	1.383(4)
C(5)-C(6)	1.508(4)	C(6)–C(7)	1.529(3)
C(7)–N(2)	1.450(3)	N(2)-C(8)	1.300(3)
Cu(1)–O(2)	2.352(3)	O(2)–S(1)	1.500(2)
S(1)-C(9)	1.789(5)	S(1)-C(10)	1.788(3)
$N(1) = C_{11}(1) = N(2)$	02.7(1)	$O(2) = C_{11}(1) = N(2)$	09.1(1)
N(1) - Cu(1) - N(2) O(2) - Cu(1) - N(1)	92.7(1)	O(2) = Cu(1) = N(2) O(1) = Cu(1) = N(2)	98.1(1)
O(2) - Cu(1) - N(1)	88.4(1)	O(1) - Cu(1) - N(2)	83.0(1)
O(1)-Cu(1)-N(1)	174.8(1)	O(1)-Cu(1)-O(2)	89.3(1)
Cl(1)-Cu(1)-N(2)	158.3(1)	Cl(1)-Cu(1)-N(1)	94.7(1)
Cl(1)-Cu(1)-O(2)	102.48(7)	Cl(1)-Cu(1)-O(1)	90.36(9)
Cu(1)-O(2)-S(1)	111.4(2)	Cu(1)-N(1)-C(5)	124.7(2)
Cu(1)-N(1)-C(1)	116.8(2)	C(1)-N(1)-C(5)	118.2(3)
N(1)-C(1)-C(2)	122.6(3)	C(1)-C(2)-C(3)	119.3(4)
C(2)-C(3)-C(4)	118.8(4)	C(3)-C(4)-C(5)	120.3(3)
N(1)-C(5)-C(4)	120.8(3)	C(4)-C(5)-C(6)	120.5(3)
N(1)-C(5)-C(6)	118.7(3)	C(5)-C(6)-C(7)	113.3(2)
C(6)-C(7)-N(2)	109.8(2)	Cu(1)-N(2)-C(7)	125.7(2)
C(7)-N(2)-C(8)	120.3(2)	Cu(1)-N(2)-C(8)	114.0(2)
O(2)-S(1)-C(10)	107.5(2)	O(2)-S(1)-C(9)	106.2(2)
C(9)-S(1)-C(10)	96.2(2)		





Fig. 1. The crystal structure of trans-Pd<sub>2</sub>(A)(Cl)<sub>2</sub>.

dimethylsulphoxide or dimethylformamide. The IR spectrum of H<sub>2</sub>B shows bands at 3311 cm<sup>-1</sup> ( $\nu_{N-H}$ ) and at 1655 cm<sup>-1</sup> ( $\nu_{C=O}$ ) while the <sup>1</sup>H NMR spectrum in CDCl<sub>3</sub> shows three peaks at 8.15, 7.59 and 7.16 ppm due to the protons of the pyridine rings and a peak at 8.10 ppm attributed to the amidic protons and two peaks at 3.00 and 3.74 ppm due to the methylenic protons, the peaks at 3.74 ppm showing a coupling with the aminic proton.

The IR spectrum of H<sub>2</sub>C parallels that of H<sub>2</sub>B; the  $\nu_{N-H}$  and  $\nu_{C=O}$  lie respectively at 3276 cm<sup>-1</sup> and 1657 cm<sup>-1</sup>. The <sup>1</sup>H NMR in dmso-d<sub>5</sub> shows the amidic protons at 8.99 ppm, the aromatic protons at 7.80 ppm and the protons of the two methylenic groups at 3.31 and 3.07 ppm.

The proposed structures of  $H_2C$  and  $H_2B$  were also corroborated by FAB mass spectrometry (the parent peak at the appropriate m/z value was detected) and was confirmed by an X-ray diffractometric investigation on  $H_2B$ . Crystals of  $H_2B$ , grown from a tetrahydrofuran diethylether solution, show the asymmetric unit is formed by half a molecule of the ligand which has an inversion centre in between the carbon atoms C(8)-C(8') of the oxamidic group. A perspective view of the molecule with atom labelling is shown in Fig. 2. Selected bond lengths and angles are given in Table 6. In the cell the molecule is elongated (Fig. 3) and can be described as a three-step system, where the two lateral (or external) steps are formed by the planes of the pyridinic rings and the



Fig. 2. Perspective view of H<sub>2</sub>B.



Fig. 3. The crystal packing of H<sub>2</sub>B.

third inside step formed by the plane containing the atoms C(7), N(2), C(8), O(1) and the corresponding atoms C(7'), N(2'), C(8'), O(1') related by a symmetry inversion centre. The bond distance and angles of the pyridine rings are normal, the mean C–C and C–N distance being 1.39 Å and 1.34 Å and the angles ranging from 118 to 123°. The bond distances, containing the amidic nitrogen, are different: 1.450(3) Å for N(2)–C(7) and 1.328(3) Å for N(2)–C(8); this difference is due to partial electronic delocalization on N(2)–C(8) caused by the presence of a double bond in C(8)–O(1), (1.227(2) Å). An intermolecular hydrogen bond network is present (Fig. 3) involving N(1) (pyridinic) and N(2) (amidic) atoms (Table 6).

H<sub>2</sub>B reacts with copper(II) and nickel(II) salts in alcoholic solution to produce the homodinuclear complexes  $M_2(B)(X)_2 \cdot nS$  (X=CH<sub>3</sub>COO<sup>-</sup>, Cl<sup>-</sup>, ClO<sub>4</sub><sup>-</sup> n=1–2.5, S=H<sub>2</sub>O, EtOH).

The preparation of mononuclear complexes was also carried out. When  $H_2B$  is reacted with copper(II) or nickel(II) salts in ethanol in a 1:1 molar ratio and in the presence of triethylamine, compounds formulable as  $M(HB)(X) \cdot nS$  $(M = Cu^{2+}, Ni^{2+}; X = Cl^{-}, CH_3COO^{-}, ClO_4^{-}; n = 1-2,5;$  $S = H_2O$ , EtOH) have been obtained. These complexes could correspond to complexes of the type  $M_2(B)(H_2B)(X)_2.nS$ , in agreement with the structurally characterized  $[Cu_2(B) (H_2B)(H_2O)_2](NO_3)_2.8H_2O$ , where dinuclear entities  $[Cu_2(B)(H_2O)_2]^{2+}$  are held together in infinite zig-zag chains by the pyridyl nitrogens of neutral H<sub>2</sub>B molecules [44]. Thus we can relate to this complex structure also our prepared compounds; in fact without an X-ray structural determination the proposal of monomeric compounds of the type M(HB)X is highly questionable. For  $Ni_2(B)(H_2B)$ - $(Cl)_2$  and  $Cu_2(B)(H_2B)(ClO_4)_2 \cdot nS$  the correct 1:1 metal:chlorine ratio and the homogeneity of the samples were ascertained by SEM and EDX analyses. It must be noted that nickel(II) forms these complexes more easily than copper(II). Thus nickel(II) chloride and acetate form complexes formulable as  $Ni_2(B)(H_2B)(X)_2$  while, under similar conditions, copper(II) chloride and acetate give rise to  $Cu_2(B)$ - $(X)_2$ ; only  $Cu(ClO_4)_2$  can produce  $Cu_2(B)(H_2B)$ - $(ClO_4)_2 \cdot nS$ . The dinuclear complexes  $M_2(B)(X)_2$  show a strong and sharp IR absorption at  $\approx 1620-1630$  cm<sup>-1</sup> due to the amide I band (1654  $\text{cm}^{-1}$  in H<sub>2</sub>B). Similar IR spectra occur also for  $M_2(B)(H_2B)(X)_2$  where a peak (or a shoulder) at  $\approx 3190 - 3150 \text{ cm}^{-1}$  due to  $\nu_{\text{NH}}$  (3310 cm<sup>-1</sup> in the free ligand) can be detected. Moreover there is a broadening of the absorption at  $\approx 1530-1525$  cm<sup>-1</sup>, which may be diagnostic of the presence of  $H_2B$  [44,45]. These data seem to corroborate the formulation proposed, but it must be emphasized that the IR spectra do not show the clear evidence found in the recent literature [44,45].

In the complexes  $Ni_2(B)(CH_3COO)_2$  and  $Cu_2(B)-(CH_3COO)_2$  intense absorptions around 1606–1600 cm<sup>-1</sup> and at 1340–1310 cm<sup>-1</sup> due respectively to the antisymmetric and symmetric stretching of the COO group are detectable. The relative intensities of the two bands suggest that the

acetate groups may act as a unidentate or a highly unsymmetrical bidentate. In the perchlorate complex  $Cu_2(B)(ClO_4)_2 \cdot nS$  strong absorptions at 1145 1091 and 1035 cm<sup>-1</sup> are indicative of perchlorate groups possibly interacting with the central metal ion. Finally in the complex Ni<sub>2</sub>(B)(Cl)<sub>2</sub>  $\nu_{Ni-Cl}$  lies at 323–325 cm<sup>-1</sup>.

In the related complexes  $Ni_2(B)(H_2B)(CH_3COO)_2$  a strong absorption at 1600 cm<sup>-1</sup> ( $\nu_{symm}$  COO) and less intense band at 1330 cm<sup>-1</sup> also suggest the acetate groups act as monodentate or as largely asymmetric chelates. In the  $Cu_2(B)(H_2B)(ClO_4)_2(EtOH)_2$  a strong band centred at 1091 cm<sup>-1</sup>, due to an almost ionic  $ClO_4^-$  group, is clearly detectable.

The nickel(II) complexes, when used as 'ligands' in the formation of heteropolynuclear complexes, undergo a transmetallation reaction; thus when the light-brown complex  $Ni_2(B)(H_2B)(Cl)_2$  is reacted, in alcoholic solution, with copper(II) salts (i.e.  $CuCl_2 \cdot nH_2O$ ), the green homodinuclear complex  $Cu_2(B)(Cl)_2$  is formed. In contrast, when  $Cu_2(B)(H_2B)(ClO_4)_2$  is reacted with  $NiCl_2 \cdot 6H_2O$ , no transmetallation occurs and the dinuclear  $Cu_2(B)(Cl)_2$  complex is obtained. These reactions can conveniently be followed by SEM and EDX analyses. The final green dicopper(II) product shows a very high homogeneity with a Cu:Cl ratio of 1:1, while signals due to nickel(II), detected in the starting complex by EDX in a 1:1 nickel:chlorine ratio, are completely absent.

These results also indicate the difficulty in obtaining heterodinuclear complexes containing copper(II) and nickel(II). All the reactions produce completely or predominantly the homodinuclear copper(II) complexes. Thus using only mild conditions and Ni(ClO<sub>4</sub>) a small amount of the heterodinuclear complex  $CuNi(B)(ClO_4)_2(H_2O)_2EtOH$ has been obtained and characterized; the major product remains the unreacted starting complex  $Cu_2(B)(H_2B)$ - $(ClO_4)_2$ . In particular when reacted with Ni $(ClO_4)_2$  in acetonitrile at room temperature,  $Cu_2(B)(H_2B)(ClO_4)_2$  reacts partially to form the heterodinuclear complex CuNi- $(B)(ClO_4)_2(H_2O)_2EtOH$ ; the residue obtained from the acetonitrile solution, evaporated to dryness, contains the starting mononuclear complex, the heterodinuclear copper(II)nickel(II) complex, Ni(ClO<sub>4</sub>)<sub>2</sub> and other unidentified products. The dissolution of the mixture in ethanol and subsequent addition of diethyl ether precipitates  $Cu_2(B)(H_2B)(ClO_4)_2$ , as ascertained by elemental analyses and IR spectroscopy. SEM and EDX investigations reveal that the copper:chlorine ratio is 1:1 with a negligible presence of nickel(II). From the mother liquor a pale blue complex was recovered. It appears to be a true heterodinuclear copper(II)-nickel(II) complex formulable as  $CuNi(B)(ClO_4)_2(H_2O)_2EtOH$ . The SEM and EDX analyses indicate the compound is homogeneous with a Cu:Ni:Cl ratio of 1:1:2.

The dinuclear entity of the homodinuclear copper(II) complexes was ascertained by single crystal X-ray diffractometry on green crystals of  $Cu_2(B)(Cl)_2(dmso)_2$ , obtained by slow crystallization of  $Cu_2B(Cl)_2$  from a dimethylsul-



Fig. 4. The crystal structure of Cu<sub>2</sub>(B)(Cl)<sub>2</sub>(dmso)<sub>2</sub>.

phoxide solution saturated with diethylether. The crystals are not stable in air but do not suffer appreciate decomposition when kept in their mother liquor. Thus the X-ray data collection was carried out by introducing the crystal and its mother liquor into a sealed quarz capillary. A perspective view of the complex with atom labelling is shown in Fig. 4; selected bond lengths and angles are given in Table 7. As found for the ligand H<sub>2</sub>B, and the Pd complex, the asymmetric unit is formed by half of the complex, owing to the presence of an inversion centre between the carbon atoms C(8)-C(8') of the oxamidic group. The ligand in the trans configuration behaves as a hexadentate dinegative compartmental dinucleating agent: each copper(II) ion is bound by a pyridine nitrogen, an oxygen and a nitrogen atom of the oxamidic group of one compartment of the ligand. A chlorine atom and an oxygen atom of a dimethylsulphoxide molecule complete the coordination polyhedron around the central metal ion. Thus each copper(II) atom is pentacoordinated and the coordination polyhedron may be best described as a distorted square planar pyramid, with the oxygen of the dimethylsulphoxide occupying the axial position.

The Cu-N(1) (pyridine) bond distance is longer that of (2.019(2) Å)than Cu-N(2)(amidic) (1.962(2) Å); this is because the amidic nitrogen is negatively charged. The Cu-Cl distance is 2.269(1) Å while the Cu–O(1) distance is 2.007(2) Å and the Cu–O(2)(dmso) is 2.352(3) Å. The copper atom is 0.169 Å above the mean plane formed by basal plane O(1), Cl(1), N(1) and N(2)towards the apical O(2) oxygen of the dimethylsulphoxide. The ligand gives rise with the metal ion to a six-membered ring (N(1), C(5), C(6), C(7), N(2), Cu) forming an N(1)–Cu–N(2) angle of 92.7(1)° and a five-membered ring (N(2), C(8), C(8'), O(1), Cu) forming a N(2)–Cu–O(1) angle of  $83.0(1)^\circ$ . The other bond distances and angles within the ligand are normal.

The magnetic moment at room temperature provides useful information about the magnetic exchange between paramagnetic centres in the prepared complexes. Thus for  $Cu_2(B)(H_2B)(ClO_4)_2$  a  $\mu_B = 1.69$  BM was found while  $Cu_2(B)(Cl)_2$  shows a  $\mu_B = 1.19$  BM for the copper atom,

indicating that an antiferromagnetic interaction takes place between the two copper(II) ions. Very likely an antiferromagnetic interaction is operating also in  $Cu_2(B)(CH_3COO)_2$ where a  $\mu_{\rm B} = 1.34$  BM for copper atom was found. The magnetic behaviour proposed for the prepared complexes must be considered with great caution. We can anticipate that for  $Cu_2(B)(Cl)_2(dmso)_2$ , according to its X-ray structure, only an intradimer interaction is operating. This conclusion cannot be extended to the other copper(II) complexes  $Cu_2(B)(Cl)_2$ and  $Cu_2(B)(Ac)_2$  where  $Cl^-$  and  $Ac^-$  may serve as binding ligands between dimers giving rise to polynuclear complexes. Obviously dmso in  $Cu_2(B)(Cl)_2(dmso)_2$  does not act as bridging ligand and favours a discrete dinuclear entity as already found for similar compounds. Attempts to grow crystals suitable for X-ray determinations were unsuccessful, and the magnetic behaviour of these complexes over a temperature range (from liquid helium to room temperature) is currently under investigation.

The magnetic moments of the nickel(II) complexes  $(\mu_B = 2.5 \text{ BM for Ni}_2(B)(H_2B)(Cl)_2 \text{ and } \mu_B = 2.8 \text{ BM for Ni}_2(B)(H_2B)(CH_3COO)_2 \text{ are lower than expected and may be due to an antiferromagnetic interaction between the two nickel(II) ions in the dinuclear entity. The corresponding homodinuclear Ni_2(B)(Cl)_2 and Ni_2(B)(CH_3COO)_2 complexes show magnetic moments of <math>\mu_B = 2.8 \text{ BM}$  and  $\mu_B = 4.2 \text{ BM}$ , respectively. An antiferromagnetic interaction may be proposed for Ni\_2(B)(Cl)\_2; a more complicated structure, possibly involving bridging acetate groups between different dinuclear entities, may exist for Ni\_2(B)(CH\_3COO)\_2. Again a correct explanation of the magnetic behaviour of these nickel(II) complexes is precluded by the lack of structural information.

Susceptibility measurements over a temperature range together with attempts to grow good crystals for further Xray investigations are currently under way in order to evaluate more conveniently the magneto-structural correlations in these systems.

Surprisingly  $H_2C$  does not react with transition metal salts: when reacted with copper(II) and nickel(II) acetate or chloride or with *trans*-Pd(C<sub>6</sub>H<sub>5</sub>CN)<sub>2</sub>(Cl)<sub>2</sub>, the starting ligand can be recovered in an almost quantitatively yield. Owing to the low solubility of  $H_2C$  in the common organic solvents, the reactions were carried out in hot dimethylformamide; probably these experimental conditions do not favour the formation of complexes, neither when soft metal ions such as palladium(II) are used.

In conclusion, the data obtained show that it is easy to obtain homodinuclear complexes. The formation of *trans*-homodinuclear species is governed mainly by the configuration of the ligands which are very probably *trans*, this suggestion being confirmed for H<sub>2</sub>B by an X-ray structural investigation.

As expected, the oxamidic group is a good mediator of magnetic exchange, consequently these systems can conveniently be proposed for studies of magnetically interacting systems. In these complexes the presence of a solvent molecule directly bonded to the copper(II) ion, filling the fifth coordination site of the square-pyramidal geometry about the central metal ion, prevents the formation of polymeric zigzagging chains and favours the formation of discrete dinuclear entities. If this solvent molecule is removed (for instance by heating), a polymeric complex is very probably synthesized which, in turn, may give rise to the dinuclear species by treatment with coordinating solvents. Thus an easy dinuclear–polynuclear process may be obtained and the variation of the physico-chemical properties associated with these reactions investigated in detail. Studies on these reactions are currently in progress.

### Acknowledgements

We thank Mrs O. Biolo, Mr A. Aguiari and E. Bullita for experimental assistance in the preparation of the ligands and complexes and in their characterization. We are indebted to Progetto Strategico, CNR 'Tecnologie Chimiche Innovative' for financial support.

#### References

- [1] P. Guerriero, S. Tamburini and P.A. Vigato, *Coord. Chem. Rev.*, 139 (1995) 17.
- [2] O. Kahn, Struct. Bonding, 68 (1987) 89; R.D. Willet, D. Gatteschi and O. Kahn, Magneto-structural Correlations in Exchange Coupled Systems, NATO ASI Series C140, Reidel, Dordrecht, 1983.
- [3] D. Gatteschi, O. Kahn, J.S. Miller and F. Parlacio, *Magnetic Molecular Materials*, NATO ASI Series, Vol. 198, Kluwer, Dordrecht, 1991.
- [4] T.M. Sorell, *Tetrahedron*, 45 (1989) 3.
- [5] O. Kahn, Molecular Magnetism, VCH, New York, 1993.
- [6] D.E. Fenton, in A.G. Sykes (ed.), Advances in Inorganic and Bioinorganic Mechanisms, Vol. 2, Academic Press, London, 1983, p. 187.
- [7] K.D. Karlin and J. Zubieta, Copper Coordination Chemistry and Biochemistry: Biochemical and Inorganic Perspectives, Adenine, Guilderland, New York, 1983.
- [8] K.D. Karlin and J. Zubieta, *Biological and Inorganic Copper Chemistry*, Vols. 1 and 2, Adenine, Guilderland, New York, 1986.
- [9] F.L. Urbach, in H. Sigel (ed.), *Metal Ions in Biological Systems, Copper Proteins, No. 13*, Marcel Dekker, Basel, 1981, p. 73, and references cited therein.
- [10] L. Que, Jr., Metal Clusters in Protein, ACS Symp. Ser., 372 (1988).
- [11] Bencini, M. Di Varia, C. Fabretti, D. Gatteschi and Z. Zanchini, *Inorg. Chem.*, 23 (1984) 1620.
- [12] J. Ribas, A. Garcia, R. Costa, M. Monfort, S. Alvarez, C. Zanchini, Y. Solans and M.V. Domenech, *Inorg. Chem.*, 30 (1991) 841.
- [13] O. Kahn, Angew. Chem., Int. Ed. Engl., 24 (1985) 834.
- [14] V.G. Albano, C. Castellari, A.C. Fabretti and A. Giusti, *Inorg. Chim. Acta*, 191 (1992) 213.

- [15] Y. Journaux, J. Sletten and O. Kahn, Inorg. Chem., 25 (1986) 439.
- [16] F. Lloret, Y. Journaux and M. Julve, Inorg. Chem., 29 (1990) 3967.
- [17] H. Ojima and K. Nonoyama, Coord. Chem. Rev., 92 (1988) 85.
- [18] A. Bencini, C. Benelli, A.C Fabretti, G. Franchini and D. Gatteschi, *Inorg. Chem.*, 25 (1986) 1063.
- [19] F. Lloret, M. Julve, J.A. Real, J. Faus, R. Ruiz, M. Mollar, I. Castro and C. Bois, *Inorg. Chem.*, 31 (1992) 2956.
- [20] F. Lloret, M. Julve, J. Faus, R. Ruiz, I. Castro, M. Mollar, M. Philoche-Levisalles and C. Bois, *Inorg. Chem.*, 31 (1992) 784.
- [21] A. Escuer, R. Vicente, J. Ribas, R. Costa and X. Solans, *Inorg. Chem.*, 31 (1992) 2627.
- [22] C. Mathonière, O. Kahn, J.-C. Daren, H. Hilbig and F.H. Kohler, *Inorg. Chem.*, 32 (1993) 40.
- [23] Y. Journaux, J. Sletten and O. Kahn, Inorg. Chem., 24 (1985) 4063.
- [24] A.C. Fabretti, A. Giusti, V.G. Albano, C. Castellari, D. Gatteschi and R.J. Sessoli, J. Chem. Soc., Dalton Trans., (1991) 2133.
- [25] C. Benelli, A.C. Fabretti and A. Giusti, J. Chem. Soc., Dalton Trans., (1993) 409.
- [26] A. Cornia, A.C. Fabretti, F. Ferraro, D. Gatteschi and A. Giusti, J. Chem. Soc., Dalton Trans., (1993) 3363.
- [27] M. Verdaguer, O. Kahn, M. Julve and A. Gleizes, *Nouv. J. Chim.*, 9 (1985) 325.
- [28] F. Lloret, J. Sletten, R. Ruiz, M. Julve, J. Faus and M. Verdaguer, *Inorg. Chem.*, 31 (1992) 778.
- [29] K. Nakatani, J. Sletten, S. Halut-Desporte, S. Jeannin and Y. Jeannin, *Inorg. Chem.*, 30 (1991) 164.
- [30] Y. Pei, O. Kahn, K. Nakatani, E. Codjovi, C. Nathoniere and J. Sletten, J. Am. Chem. Soc., 113 (1991) 6558.
- [31] Y. Pei, O. Kahn, J. Sletter, J.-P. Renard, R. Georges, J.-C. Gianduzzo, J. Curely and R. Xu, *Inorg. Chem.*, 27 (1988) 47.
- [32] K. Nakatani, J.Y. Carriat, Y. Journaux, O. Kahn, F. Lloret, J.P. Renard, Y. Pei, J. Sletten and M. Verdaguer, J. Am. Chem. Soc., 111 (1989) 5739.
- [33] D.D. Perrin, W.L.F. Armarego and D.R. Perrin, *Purification of Laboratory Chemicals*, Pergamon, Oxford, 2nd edn., 1980.
- [34] M.S. Kharesh, R.C. Seyer and F.R. Mayo, J. Am. Chem. Soc., 60 (1938) 882.
- [35] S. Taniguchi, Bull. Chem. Soc. Jpn., 57 (1984) 2683.
- [36] H.J. Chang and O. Vogl, J. Polym. Sci., 15 (1977) 311.
- [37] A.C.T. North, D.C. Phillips and F.S. Mathews, *Acta Crystollogr., Sect. A*, 24 (1968) 351.
- [38] G.M. Sheldrick, in G.M. Sheldrick, C. Kruger and R. Goddard (eds.), *Crystallographic Computing 3*, Oxford University Press, Oxford, 1985, p. 175.
- [39] P. Guerriero, P.A. Vigato and B. Burtet-Fabris, *Inorg. Chim. Acta*, 16 (1989) 155.
- [40] P.P. Morgan, J.M. Beynon, R.M. Bateman and B.M. Green, Int. J. Mass Spectrom. Ion Phys., 28 (1978) 171.
- [41] M. Barber, R.S. Bordoli, R.D. Sedgwick and A.M. Taylor, J. Chem. Soc., Chem. Commun., 7 (1981) 171.
- [42] C.J. Connor, E. Sinn, E.J. Cukauskas and B.S. Deaver, *Inorg. Chim. Acta*, 32 (1979) 29.
- [43] C.J. Connor, Progr. Inorg. Chem., 29 (1982) 203.
- [44] F. Lloret, M. Julve, J. Faus, Y. Journaux, M. Philoche-Levisalles and J. Jeannin, *Inorg. Chem.*, 28 (1989) 3702.
- [45] J.L. Sanz, B. Cervera, R. Ruiz, C. Bois, J. Faus, F. Lloret and M. Julve, J. Chem. Soc., Dalton Trans., (1996) 1359.