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Metal carbacylamidophosphates: ability of coordination patterns to di- and polymerization

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Abstract

Cobalt(II), nickel(II) and copper(II) complexes with carbacylamidophosphate ligands $\{Cl_3C(O)NP(O)R_2\}^-$ (R = OMe, NEt_2, $NHCH_2Ph$, *N*-morpholyl) were characterized by means of X-ray diffraction, IR, UV–Vis spectroscopy and thermal analysis. The organic ligands were coordinated via oxygen atoms of phosphoryl and carbonyl groups forming six membered chelate cycles. The molecular units $M\{L\}_2$ reveal ability for self-association and readily yield different di- and polymeric motifs either by μ^2-phosphorylic bridges, donor atoms of the morpholine substitute or employing an additional bridging ligand. Cobalt and nickel solvates $[M\{L\}_2(Pr^iOH)]_2$ exist as characteristic dimers sustained by phosphoryl bridges between octahedral metal atoms, while copper complexes aggregate through self-complementary Cu–O interactions with a morpholine substitute forming one-dimensional chains $[Cu\{L\}_2]_n$ or dimers $[Cu\{L\}_2(Pr^iOH)]_2$ involving terminal 2-propanol ligands. The configuration of binding sites for $[Cu\{L\}_2]$ (R = *N*-morpholyl) favors the densest pairwise association of the molecules with Cu–O (morpholine) at approximately 2.55 Å.

Keywords: Carbacylamidophosphates; Phosphorylic ligands; Self-complementary molecules; Supramolecular chemistry

1. Introduction

Construction of superstructures using self-complementary molecular subunits has recently received a great deal of attention in the context of materials science [1–4]. In this case assembly of the structure requires only one component which is capable of association employing a set of donor and acceptor sites that are already present in the molecule frame. This situation is most clearly demonstrated for different hydrogen bonded self-assembly structures [5–8]. Important examples for aggregation of molecular units by self-complementary coordination interactions are provided by metal(II) β-diketonates. The complexes ML_2 (M = Co, Ni) themselves tend to polymerize using coordination positions at the octahedral metal atoms [9–11], but incorporation of additional donor substitutes in the ligand frame allows to generate a novel self-complementary system for the needs of supramolecular synthesis. Especially attractive targets are metal diketonates bearing donor pendants (pyridyl or etheric) at the available positions on the carbon atoms. These complexes in the solid state aggregate giving superstructures with useful functional properties including molecular magnets [12] and porous host lattices with zeolite behavior [3,4]. The monomeric and oligomeric species also could provide suitable configuration of binding sites for various substrates and hence to promote or catalyze chemical reactions. For example, simple metal diketonates catalyze symmetrization of organomercury compounds and the intermediates of the reaction exist in the form of a complex mixed-metal aggregate [13].

We were interested in the generalization of these observations and in expansion of the above strategy to heteroanalogs of β-diketonates [14], in particular to phosphoryl substituted ligands of the carbacylamido-

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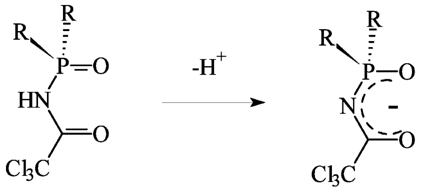
phosphate family. Coordination chemistry of carbacylamidophosphates has many analogies in the realm of β-diketonates and provides examples for most characteristic coordination motifs including different dimeric patterns [15], cubane-like clusters [16] and octahedral tris-complexes [17,18]. These ligand systems represent novel paradigms for the synthesis of poly- and oligomeric self-assembly metal chelates and combine high affinity to transition metal ions with structural simplicity and chemical accessibility. The structure of the ligands offer rich and versatile possibilities for their further functionalization by fine tuning the properties of the substitutes at the phosphorus atom where a suitable group could be immobilized by very simple nucleophilic reactions. In this contribution we report metal carbacylamidophosphates that display different modes of association that take place either by μ^2-phosphorylic bridges, donor atoms of the substitutes or an additional neutral ligand.

2. Results and discussion

Coordination compounds were prepared employing carbacylamidophosphate ligands with variation of substitutes at the phosphorus atom:



$H\{L^1\}$: $R = \text{-NHCH}_2\text{Ph}$
$H\{L^2\}$: $R = \text{-N(CH}_2\text{CH}_2)_2\text{O}$
$H\{L^3\}$: $R = \text{-N(C}_2\text{H}_5)_2$
$H\{L^4\}$: $R = \text{-OCH}_3$

In all Co(II), Ni(II) and Cu(II) complexes the organic ligands were coordinated bidentately via oxygen atoms of phosphoryl and carbonyl groups forming six membered chelates. These metallocycles in all cases are appreciably planar with the atoms deviating from the chelate mean plane by approximately 0.1–0.3 Å.

Metal(II) carbacylamidophosphates are neutral species with unsaturated functionality of octahedral metal ions that readily coordinate additional bidentate chelate donor groups (e.g. 2,2′-bipyridine, phenanthroline). This behavior has close precedents in β-diketonate coordination chemistry [19]. Recrystallization of the carbacylamidophosphate compounds from dimethylsulfoxide could also provide molecular octahedral complexes of the type $[\mathrm{M(L)_2(DMSO)_2}]$, but in less donor media saturation of the coordination functionality takes place rather through self-association of the complex units. This is contrary to the β-diketonate analogs. The latter ones also form different di- and oligomeric molecules $[\mathrm{M}\{\mathrm{L}\}_2]_n$ that, however, readily degradate in solutions yielding the usual octahedral $[\mathrm{M}\{\mathrm{L}\}_2(\mathrm{Solv})_2]$ complexes [20,21].

The first principal possibility for aggregation of metal carbacylamidophosphates is nucleation facilitated by the bridging function of PO and/or CO oxygen atoms. In fact under the absence of strong neutral donors the compounds adopt a very characteristic dimeric pattern as was illustrated by examination of $[\mathrm{Co}\{\mathrm{L}^1\}_2(\mathrm{Pr}^i\mathrm{OH})]_2$ (**1**), $[\mathrm{Ni}\{\mathrm{L}^1\}_2(\mathrm{Pr}^i\mathrm{OH})]_2$ (**2**) and $[\mathrm{Ni}\{\mathrm{L}^4\}_2(\mathrm{Pr}^i\mathrm{OH})]_2$ (**3**). Cobalt and nickel complexes **1** and **2** are isostructural and exist as molecular dimeric species. These dimers are actually centrosymmetric (Fig. 1) and the centroid of the $\mathrm{M_2O_2}$ quadrangle occupies a center of quasiinversion at (0, 1/4, 1/4). Slightly different orientation of bulk benzyl substitutes on a periphery of the molecule lowers the entire symmetry that results in doubling of the cell. The structures could be solved in the same space group with a twice less unit cell volume and refined to poor convergence with irresoluble disorder for part of the benzyl linkage. Nickel complex **3** (Fig. 2) clearly illustrates this situation as the compound is also isostructural with the cobalt analog [15] but due to a more symmetric orientation of methoxy groups at the phosphorus atoms it has a twice less unique part.

According to UV–Vis spectra, metal atoms of the compounds preserve their coordination environment in 2-propanol solution. The diffusion reflectance and absorption data are practically identical and are characteristic of Co(Ni) octahedral complexes. Thus for $[\mathrm{Co}\{\mathrm{L}^1\}_2(\mathrm{Pr}^i\mathrm{OH})]_2$ (**1**) the band respective to the transition $^4\mathrm{T}_{1g}(\mathrm{P}) \rightarrow {}^4\mathrm{T}_{1g}$ was observed near 19 130 cm^{-1}, for the nickel analog **2** the $^3\mathrm{A}_{2g} \rightarrow {}^3\mathrm{T}_{1g}(\mathrm{P})$ transition band was found at 24 650 cm^{-1}.

The dimeric structure of the compounds is supported by the bridging function of only the phosphorylic oxygen atom. Such discrimination of a carbonyl donor center is evident due to a higher affinity of the metal ions to the phosphorylic ligands and in the present case it is not influenced by varying the steric volume of substitutes at the phosphorus atom. This situation is also reflected by somewhat longer bond distances M–O(C) in comparison with M–O(P) (monodentate) (2.01 vs.

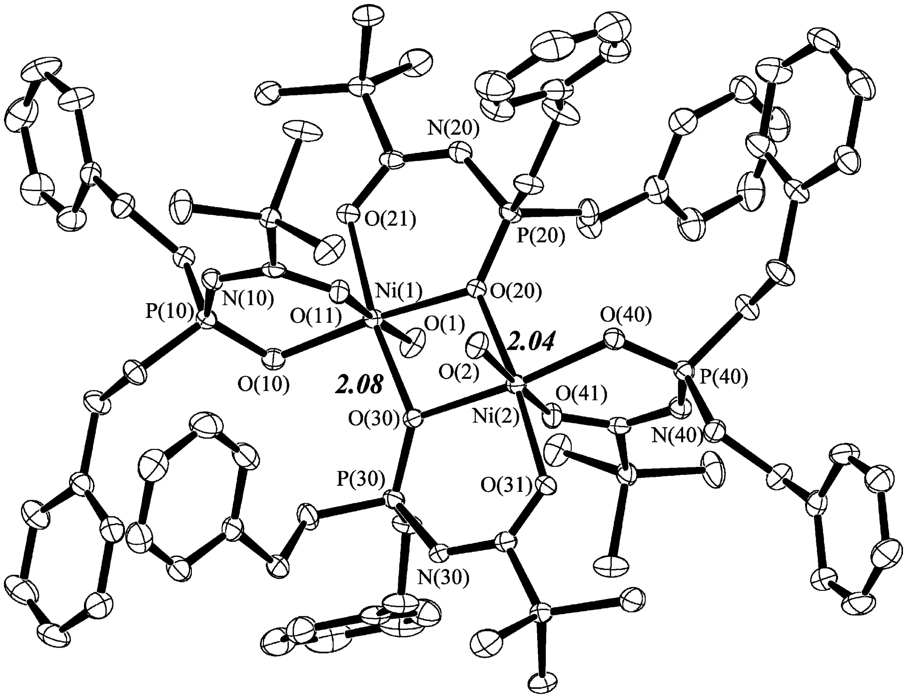


Fig. 1. Dimeric structure of the $[\mathrm{Ni}\{\mathrm{L}^1\}_2(\mathrm{Pr}^i\mathrm{OH})]_2$ (**2**) complex (carbon atoms of 2-propanol are omitted) showing bridging functions of P(20)–O(20) and P(30)–O(30) groups between two metal atoms. Note that the dimer is actually centrosymmetric and only orientation of benzyl groups at P(20) and P(30) precludes generation of a center of inversion. Thermal ellipsoids are at the 50% level. $[\mathrm{Co}\{\mathrm{L}^1\}_2(\mathrm{Pr}^i\mathrm{OH})]_2$ (**1**) complex is isomorphous.

2.04 Å, Table 2). In **1** and **2** all phosphorylic oxygen atoms are situated in the equatorial plane of the dimer: all of them are involved into a six membered chelate metalocycle and two of four PO groups also bridge two metal atoms. The presence of two unequal phosphorylic groups in the compounds has reflectance in IR spectra revealing two bands ν(P=O) that differ in approximately 20 cm^{-1} (Table 1). These bands are sensitive to the coordination and for all examined compounds ν(P=O) are essentially lower than ones for ionic alkali metal salts ($\Delta_{\nu(\mathrm{P=O})}$ 40–100 cm^{-1}).

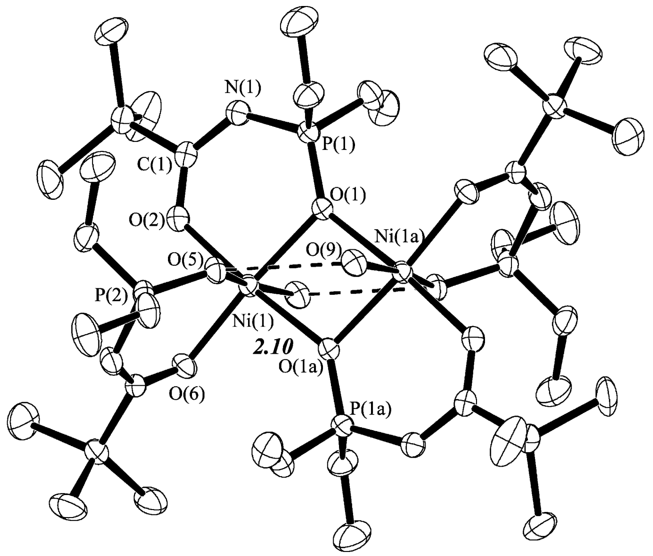


Fig. 2. Centrosymmetric dimeric molecule of $[\mathrm{Ni}\{\mathrm{L}^4\}_2(\mathrm{Pr}^i\mathrm{OH})]_2$ (**3**) (carbon atoms of 2-propanol are omitted). Thermal ellipsoids are at the 40% level. Possible hydrogen bonding between coordinated 2-propanol and phosphorylic groups is shown with dotted lines (O···O 2.83 Å).

Two remaining axial positions at the metal atoms are occupied by molecules of 2-propanol. This ligand provides also a hydrogen bond donor for interaction with the axial oxygen atom at an adjacent metal center thus additionally stabilizing the dimeric core. In the $[\mathrm{Ni}\{\mathrm{L}^4\}_2(\mathrm{Pr}^i\mathrm{OH})]_2$ (**3**) complex these axial positions are occupied by phosphoryl groups that form a relatively strong H-bond (O···O 2.83 Å). In this case the phosphorylic group also demonstrates more nucleophylic character, but in this respect the topology of the dimer appears to be tunable. In compounds **1** and **2** that possess bulky benzyl substitutes at the phosphorus atoms these axial positions are occupied by carbonyl groups. The hydrogen bonding with the 2-propanol molecule is very weak and is effective at only one side of the dimer (O···O 2.94 and 3.20 Å).

Thermal behavior of compounds **1** and **2** is similar: loss of coordinated 2-propanol was detected at 140–195 °C. It has an appreciable exothermic effect that may be attributed to polymerization or isomerization of the complex after elimination of the neutral ligand. Complex $[\mathrm{Ni}\{\mathrm{L}^4\}_2(\mathrm{Pr}^i\mathrm{OH})]_2$ looses 2-propanol stepwise at 135–185 °C and 210–240 °C and that was followed by exothermic decomposition at 260 °C.

Table 1
Main IR absorption bands and their assignments for carbacylamidophosphate compounds, cm^{-1}

Compound	ν(P=O)	$\Delta_{\nu(\mathrm{P=O})}$ [a]	ν(C=O)	$\Delta_{\nu(\mathrm{C=O})}$ [a]	ν(C–N)	ν(O–H)
$\mathrm{H\{L^1\}}$	1250	+96	1709	+107	1455	
$\mathrm{Na\{L^1\}}$	1154		1602		1336	
$[\mathrm{Co\{L^1\}_2(Pr^{\mathit{i}}OH)}]_2$ (**1**)	1070, 1090	−84 −64	1610	+8	1345	3340, 3390
$[\mathrm{Ni\{L^1\}_2(Pr^{\mathit{i}}OH)}]_2$ (**2**)	1075, 1090	−79 −64	1620	+18	1350	3350, 3380
$\mathrm{H\{L^2\}}$	1201	+38	1728	+107	1450	
$\mathrm{Na\{L^2\}}$	1163		1621		1344	
$\mathrm{Cu\{L^2\}_2}$ (**4**)	1080, 1120	−83 −43	1605	−16	1360	
$[\mathrm{Cu\{L^2\}_2(Pr^{\mathit{i}}OH)}]_2$ (**5**)	1090, 1115	−73 −48	1610, 1625	−11 +4	1370	3410
$\mathrm{H\{L^3\}}$	1235	+105	1725	+100	1480	
$\mathrm{Na\{L^3\}}$	1130		1625		1335	
$[\mathrm{Cu\{L^3\}_2}]_2\cdot$Diox (**6**)	1028, 1086	−102 −54	1602, 1622	−23 −3	1340	
$\mathrm{Cu\{L^3\}_2\cdot 2Pr^{\mathit{i}}OH}$ (**7**)	1026, 1085	−104 −55	1599, 1628	−26 +3	1357	3429

[a] Shift of the absorption maximum with respect to the value for the corresponding ionic salt.

As in the case of metal β-diketonates, presence of efficient donors in the solution prevents formation of dimeric species based upon carbacylamidophosphates. Especially this is the case for copper(II) ions forming only four close coordination contacts under typical 4+2 or 4+1 coordination. However, when a bridging neutral

Table 2
Geometry of the metal ion coordination environment (Å, °) for dimeric complexes $[\mathrm{M\{L\}_2(Pr^{\mathit{i}}OH)}]_2$

$[\mathrm{Co\{L^1\}_2(Pr^{\mathit{i}}OH)}]_2$ (**1**) and $[\mathrm{Ni\{L^1\}_2(Pr^{\mathit{i}}OH)}]_2$ (**2**)			
	Co	Ni	
Bond lengths			
M(1)–O(10)	2.028(2)	2.009(2)	
M(1)–O(20)	2.044(2)	2.022(2)	
M(1)–O(11)	2.066(2)	2.037(2)	
M(1)–O(1)	2.075(2)	2.055(2)	
M(1)–O(21)	2.125(2)	2.071(2)	
M(1)–O(30)	2.135(2)	2.084(2)	
M(2)–O(40)	2.034(2)	2.012(2)	
M(2)–O(30)	2.072(2)	2.053(2)	
M(2)–O(41)	2.075(2)	2.044(2)	
M(2)–O(2)	2.081(2)	2.059(2)	
M(2)–O(20)	2.084(2)	2.036(2)	
M(2)–O(31)	2.098(2)	2.050(2)	
Bond angles			
O–M–O chelate	90.27(9)–92.62(9)	91.88(9)–94.25(8)	
M(1)–O(20)–M(2)	101.11(9)	101.35(9)	
M(2)–O(30)–M(1)	98.51(9)	98.73(8)	
O(20)–M(1)–O(30)	79.86(9)	79.73(8)	
O(11)–M(1)–O(1)	177.51(9)	176.97(9)	
O(41)–M(2)–O(2)	175.12(9)	175.51(9)	
$[\mathrm{Ni\{L^4\}_2(Pr^{\mathit{i}}OH)}]_2$ (**3**) a: $2-x$, $-y$, $-z$			
Ni(1)–O(1)	2.058(2)	O–Ni(1)–O chelate	92.94(8), 93.28(8)
Ni(1)–O(2)	2.003(2)	Ni(1)–O(1)–Ni(1a)	97.80(8)
Ni(1)–O(1a)	2.098(2)	O(1)–Ni(1)–O(1a)	82.20(8)
Ni(1)–O(5)	2.058(2)	O(6)–Ni(1)–O(2)	91.54(9)
Ni(1)–O(6)	1.989(2)	O(1)–Ni(1)–O(5)	88.00(8)
Ni(1)–O(9)	2.063(2)	O(5)–Ni(1)–O(9)	171.37(8)

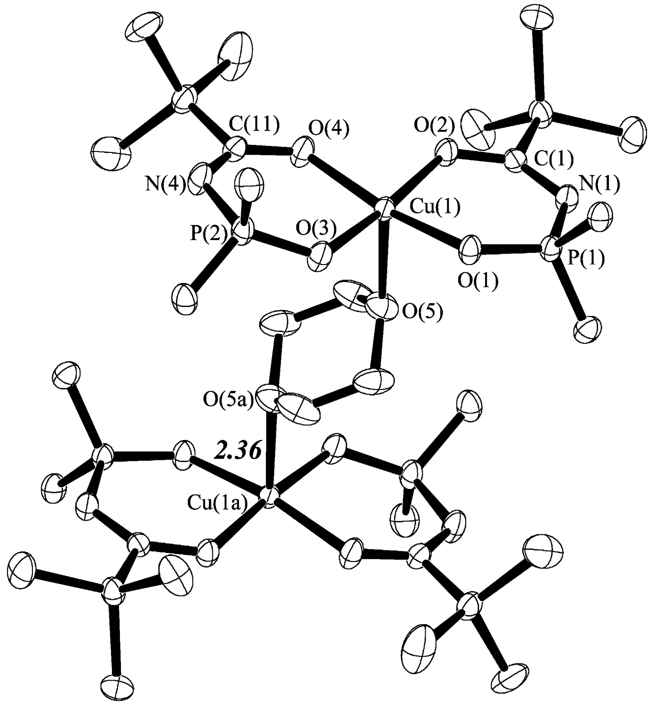


Fig. 3. $[\mathrm{Cu}\{\mathrm{L}^3\}_2]_2\cdot$Diox (**6**) complex: dinuclear structure of the molecule is supported by the bridging function of the dioxane ligand. Ethyl groups are omitted and thermal ellipsoids are drawn at the 30% probability level.

ligand is employed, it is possible to achieve aggregation of the metal complexes into dimeric molecules. Crystallization from 1,4-dioxane afforded complex $[\mathrm{Cu}\{\mathrm{L}^3\}_2]_2\cdot$ Diox **6** that displays a dimeric array formed by two $\mathrm{Cu}\{\mathrm{L}^3\}_2$ units bridged by a neutral donor molecule (Fig. 3). This dioxane molecule is bound relatively tightly with Cu–O distances (2 × 2.362(4) Å) that are characteristic for axial coordination in copper(II) complexes (Table 3). DTA data reveal loss of dioxane only at 180 °C.

Effective bridging by the dioxane molecule is interesting as functional groups of very similar donor properties may be easily integrated into the ligand frame. We have examined coordination compounds based upon the carbacylamidophosphate ligand $\mathrm{H}\{\mathrm{L}^2\}$ bearing two morpholine groups as suitable donor pendants and in this the case resulting $\mathrm{M}\{\mathrm{L}\}_2$ units may be considered as self-complementary molecules possessing bond donor and acceptor sites for aggregation in oligomeric motifs. Indeed, copper complexes tend to polymerize giving different products. Crystallization from 2-propanol led to polymeric $\mathrm{Cu}\{\mathrm{L}^2\}_2$ (**4**) compound in mixture with dimeric 2-propanol solvate $[\mathrm{Cu}\{\mathrm{L}^2\}_2(\mathrm{Pr}^i\mathrm{OH})]_2$ (**5**). In both the structures the metal atoms adopt distorted octahedral coordination. In $[\mathrm{Cu}\{\mathrm{L}^2\}_2(\mathrm{Pr}^i\mathrm{OH})]_2$ (**5**) the self-complementary units associate forming a dimer and the remaining functionality at two copper atoms was used for coordination of 2-propanol molecules. The latter ones hence terminate nucleation of the complex by propagation of the dimer. It is worth noting that the 2-propanol molecule is situated in the equatorial plane (Cu–O 2.015 Å). It is perhaps counterintuitive that one carbonyl oxygen atom of the chelate is eliminated from this plane to the apex of the bipyramidal coordination polyhedron and maintains more weak coordination contact with the copper atom (Cu–O 2.211 Å). Such disposition of the ligands evidently stabilizes the dimer as in the case of axial coordination the neutral molecule could be bound only very weakly to be an efficient terminal ligand preventing further polymerization (Fig. 4).

Presence of two unequal Cu–carbonyl bonds in $[\mathrm{Cu}\{\mathrm{L}^2\}_2(\mathrm{Pr}^i\mathrm{OH})]_2$ (**5**) has clear reflectance in IR spectra that show doubling of the ν(C=O) band (Table 1). One absorption maximum has actually the same value as for the ionic salt $\mathrm{Na}\{\mathrm{L}^3\}$, while the other is slightly shifted to a lower frequency region ($\Delta_{\nu(\mathrm{C=O})}$ -11 cm^{-1}). According to DTA data, complex $[\mathrm{Cu}\{\mathrm{L}^2\}_2(\mathrm{Pr}^i\mathrm{OH})]_2$ (**5**) in fact readily looses coordinated alcohol. Endothermic 7.5% weight loss at 98 °C indicated total elimination of 2-propanol and formation of the $\mathrm{Cu}\{\mathrm{L}^2\}_2$ compound. Further decomposition of the latter is accompanied by a vigorous exothermic oxidation at 190 °C.

The $\mathrm{Cu}\{\mathrm{L}^2\}_2$ (**4**) structure is clearly derived from the motif observed for dioxane solvate **6**: in this case two anionic ligands were coordinated in the equatorial plane with formation of six membered chelates (Cu–O are in the range 1.937(2)–1.971(2) Å) and two remaining axial sites were used for propagation of the structure. Neutral complex units $\mathrm{Cu}\{\mathrm{L}^2\}_2$ associate by two long axial contacts Cu–O with morpholine substitutes (2.545(2) and 2.564(2) Å, Fig. 5) forming a linear chain. As in the case of the dimeric pattern $[\mathrm{Cu}\{\mathrm{L}^2\}_2(\mathrm{Pr}^i\mathrm{OH})]_2$ the molecules associate pairwise which is made possible by suitable disposition of morpholine pendants at the tetrahedral phosphorus atoms and almost orthogonal orientation of the bond with an adjacent copper atom towards the plane of $\mathrm{Cu}\{\mathrm{L}^2\}_2$ units (Fig. 5). Hence the densest interconnection of the molecules is facilitated by the inherent structure of the organic ligands. The present mode of intermoiety interaction is contrary to that observed earlier for self-complementary copper diketonate molecules where configuration of the donor substitutes supports formation of a two-dimensional grid network [12] or assembly of very open molecular hexagons [3,4]. We suppose that the above copper–morpholine motif also has a significance for methodology of 'one-component supramolecular synthesis' though due to the dense pairwise association it is difficult to predict high porosity for the resulting metal-organic array.

Table 3
Selected bond length (Å) and bond angles (°) for copper complexes **4**–**6**

Bond lengths		Bond angles	
$\mathrm{Cu\{L^2\}_2}$ (**4**) a: $1-x, 2-y, 2-z$; b: $-x, 2-y, 1-z$			
Cu–O(11)	1.937(2)	P(2)–N(21)	1.637(2)
Cu–O(21)	1.950(2)	O(12)–C(10)	1.261(3)
Cu–O(22)	1.959(2)	O(22)–C(20)	1.260(3)
Cu–O(12)	1.971(2)	N(21)–C(20)	1.292(3)
Cu–O(23a)	2.545(2)	C(10)–N(11)	1.298(3)
Cu–O(13b)	2.564(2)	O(21)–Cu–O(22)	92.89(7)
P(1)–O(11)	1.506(2)	O(11)–Cu–O(12)	91.41(7)
P(2)–O(21)	1.505(2)	O(23a)–Cu–O(13b)	169.86(6)
P(1)–N(11)	1.637(2)	O(21)–Cu–O(23a)	86.11(7)
$\mathrm{[Cu\{L^2\}_2(Pr^iOH)]_2}$ (**5**)			
Cu(1)–O(5)	1.927(1)	O(2)–C(1)	1.256(3)
Cu(1)–O(2)	1.962(2)	O(6)–C(11)	1.244(3)
Cu(1)–O(1)	1.978(2)	N(1)–C(1)	1.293(3)
Cu(1)–O(6)	2.215(2)	N(4)–C(11)	1.303(3)
Cu(1)–O(9)	2.012(2)	O(2)–Cu(1)–O(1)	92.88(6)
P(1)–O(1)	1.500(2)	O(5)–Cu(1)–O(9)	89.22(7)
P(2)–O(5)	1.509(2)	O(1)–Cu(1)–O(9)	175.11(7)
P(1)–N(1)	1.630(2)	C(1)–N(1)–P(1)	123.4(2)
P(2)–N(4)	1.622(2)	C(11)–N(4)–P(2)	124.8(2)
$\mathrm{[Cu\{L^3\}_2]_2 \cdot Diox}$ (**6**)			
Cu(1)–O(3)	1.932(3)	C(1)–O(2)	1.264(5)
Cu(1)–O(1)	1.939(3)	C(1)–N(1)	1.299(5)
Cu(1)–O(2)	1.949(3)	O(4)–C(11)	1.261(5)
Cu(1)–O(4)	1.970(3)	N(4)–C(11)	1.284(6)
Cu(1)–O(5)	2.362(4)	O(1)–Cu(1)–O(2)	93.1(1)
P(1)–O(1)	1.515(3)	O(3)–Cu(1)–O(4)	92.5(1)
P(2)–O(3)	1.514(3)	O(1)–Cu(1)–O(5)	93.5(1)
P(1)–N(1)	1.647(4)	C(1)–N(1)–P(1)	122.7(3)
P(2)–N(4)	1.650(4)	C(11)–N(4)–P(2)	122.2(3)

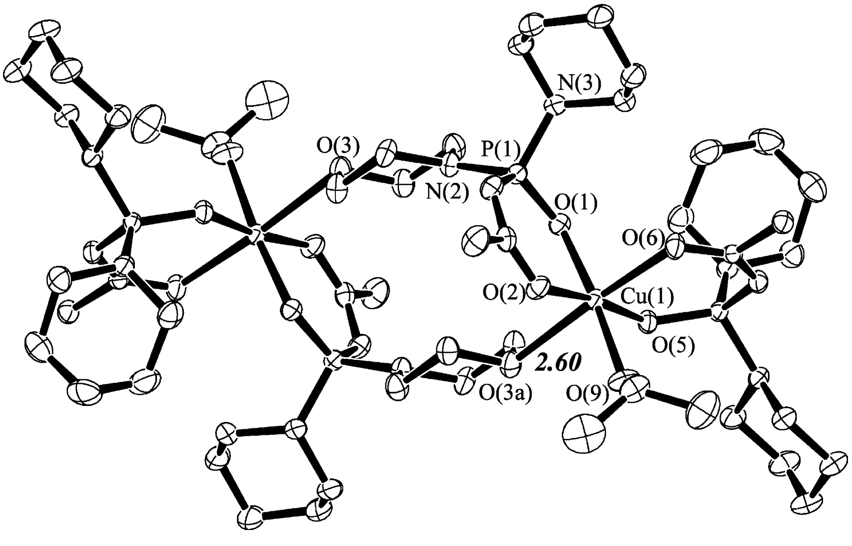


Fig. 4. View of the $\mathrm{[Cu\{L^2\}_2(Pr^iOH)]_2}$ (**5**) structure showing how two self-complementary parts associate into the dimer by means of a weak Cu–O bond with the morpholine group. Hydrogen atoms are omitted.

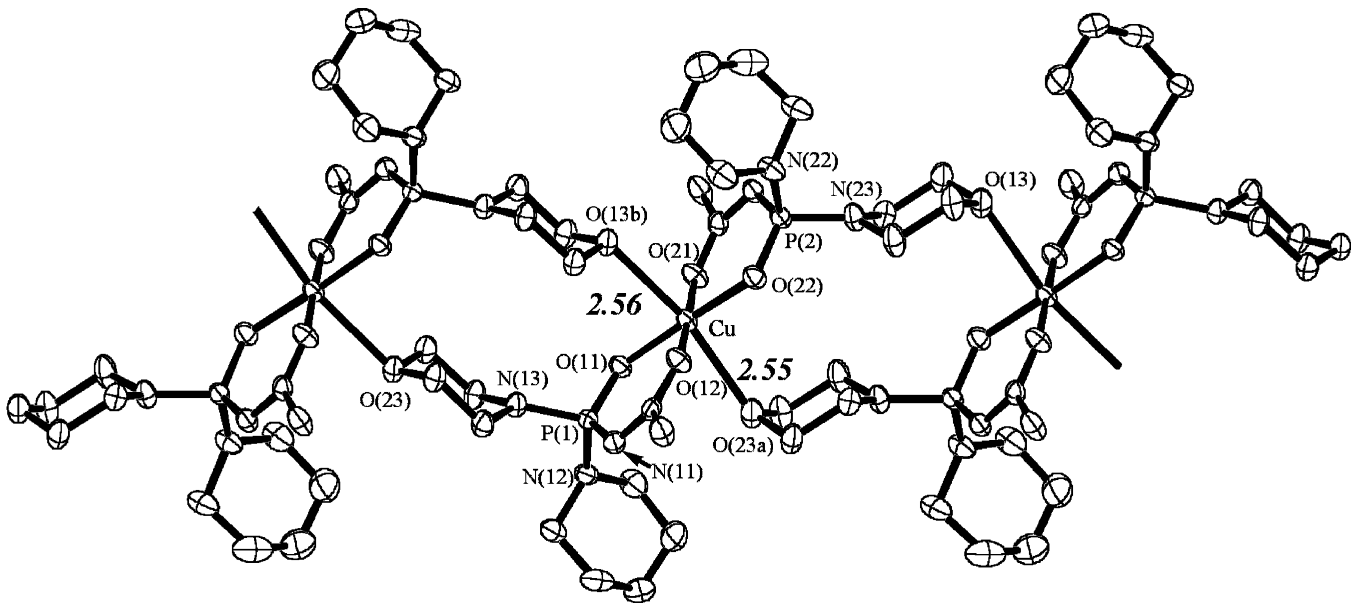


Fig. 5. Fragment of one-dimensional polymeric chain $[Cu\{L^2\}_2]_n$ (**4**) that is assembled by formation of two weak axial bonds Cu–O with the morpholine group. Hydrogen atoms are omitted.

3. Experimental

3.1. Synthesis

All the chemicals were commercial products of reagent grade, used without further purification. The ligands were prepared reacting phosphorus pentachloride with trichloroacetamide followed by addition of nucleophylic reagent (MeOH, diethylamine, morpholine, benzylamine) in accordance with general procedure [22]. Coordination compounds were synthesized in alcoholic media using anionic carbacylamidophosphates and metal nitrates or chlorides.

3.1.1. $[Co\{L^1\}_2(Pr^iOH)]_2$ (*1*)

Methanolic solutions (10 ml) of 0.105 g (1.94 mmol) sodium methylate and 0.814 g (1.94 mmol) $H\{L^1\}$ were combined and then added to 0.295 g (0.97 mmol) $Co(NO_3)_2 \cdot 6H_2O$ in 5 ml MeOH. The solution was evaporated and the residue was triturated with 2-propanol–MeOH mixture (9:1 v/v). Precipitate of $NaNO_3$ was filtered off and the filtrate was allowed to stand in a vacuum desiccator over $CaCl_2$. The pink prismatic crystals of the complex were filtered, washed with cold 2-propanol and dried in air. The yield was 1.1 g (60 %). *Anal*. Found: C, 42.22; H, 3.92; N, 8.95. Calc. for $C_{32}H_{32}Cl_6CoN_6O_4P_2$: C, 42.78; H, 3.56; N, 9.36%. The nickel complexes $[Ni\{L^1\}_2(Pr^iOH)]_2$ (**2**) and $[Ni\{L^4\}_2(Pr^iOH)]_2$ (**3**) were prepared in the same way starting with $Ni(NO_3)_2 \cdot 6H_2O$. *Anal*. for **2** Found: C, 42.24; H, 3.88; N, 8.87. Calc. for $C_{32}H_{32}Cl_6N_6NiO_4P_2$: C, 42.79; H, 3.56; N, 9.36%. Compounds are soluble in alcohols and chloroform and insoluble in water.

3.1.2. $Cu\{L^2\}_2$ (*4*) and $[Cu\{L^2\}_2(Pr^iOH)]_2$ (*5*)

0.037 g (1.6 mmol) Sodium metal was dissolved in 10 ml 2-propanol and added to 0.594 g (1.6 mmol) $H\{L^2\}$ in 2-propanol. The resulting solution of the sodium salt was added to 0.139 g (0.8 mmol) $CuCl_2 \cdot 2H_2O$ in 10 ml MeOH and precipitate NaCl was filtered out. Slow evaporation in a vacuum desiccator over dry $CaCl_2$ afforded crystalline material that consists of the mixture of $Cu\{L^2\}_2$, blue–green needles (yield approximately 60%), and $[Cu\{L^2\}_2(Pr^iOH)]_2$, light-green prisms (yield approximately 20%). The crystals were separated manually. *Anal*. for $Cu\{L^2\}_2$. Found: C, 29.14; H, 3.84; N, 10.5. Calc. for $C_{20}H_{32}Cl_6CuN_6O_8P_2$: C, 29.20; H, 3.92; N, 10.2%. *Anal*. for $[Cu\{L^2\}_2(Pr^iOH)]_2$. Found: C, 31.3; H, 4.53; N, 9.5. Calc. for $C_{20}H_{32}Cl_6CuN_6O_8P_2$: C, 29.20; H, 3.92; N, 10.2%. The compounds are well soluble in polar organics and insoluble in water.

Complexes $[Cu\{L^3\}_2]_2 \cdot$Diox (**6**) and $Cu\{L^3\}_2 \cdot 2Pr^iOH$ (**7**) were prepared in a similar fashion starting with sodium salt $Na\{L^3\}$ [23]. Ten millilitres 1,4-dioxane was added to 0.753 g (2 mmol) of the above salt and 0.175 g (1 mmol) $CuCl_2 \cdot 2H_2O$ in 2-propanol-methanolic mixture after separation of sodium chloride. This solution afforded blue–green needles of $Cu\{L^3\}_2 \cdot 2Pr^iOH$ (**7**) (0.17 g, 20%) in a mixture with green prisms of $[Cu\{L^3\}_2]_2 \cdot$Diox (0.81 g, 50%). The crystals were washed with benzene and hexane, then dried and the mixture was separated manually. *Anal*. for **6**. Found: C, 32.42; H, 5.39; N, 10.31. Calc. for $C_{20}H_{40}Cl_6CuN_6O_4P_2$: C, 31.1; H, 5.19; N, 10.9%. *Anal*. for **7**. Found: C, 33.25; H, 5.77; N, 10.11. Calc. for $C_{20}H_{40}Cl_6CuN_6O_4P_2$: C, 31.1; H, 5.19; N, 10.9%. Both the compounds are soluble in alcohols, sparingly soluble in benzene and

Table 4
Crystal data and structure refinement for $[Co\{L^1\}_2(Pr^iOH)]_2$ (**1**), $[Ni\{L^1\}_2(Pr^iOH)]_2$ (**2**), $[Ni\{L^4\}_2(Pr^iOH)]_2$ (**3**), $Cu\{L^2\}_2$ (**4**), $[Cu\{L^2\}_2(Pr^iOH)]_2$ (**5**) and $[Cu\{L^3\}_2]_2 \cdot$Diox (**6**)

	1	**2**	**3**	**4**	**5**	**6**
Empirical formula	$C_{70}H_{80}Cl_{12}Co_2N_{12}O_{10}P_4$	$C_{70}H_{80}Cl_{12}Ni_2N_{12}O_{10}P_4$	$C_{22}H_{40}Cl_{12}N_4Ni_2O_{18}P_4$	$C_{20}H_{32}Cl_6CuN_6O_8P_2$	$C_{23}H_{40}Cl_6CuN_6O_9P_2$	$C_{44}H_{88}Cl_{12}Cu_2N_{12}O_{10}P_4$
Formula weight	1916.60	1916.16	1315.28	822.70	882.79	1621.62
Temperature (K)	100	100	223	293	293	293
Crystal system	triclinic	triclinic	triclinic	triclinic	monoclinic	monoclinic
Space group	$P\bar{1}$	$P\bar{1}$	$P\bar{1}$	$P\bar{1}$	$P2_1/c$	$C2/c$
a (Å)	11.829(2)	11.830(2)	10.466(1)	10.3351(5)	18.691(1)	26.070(3)
b (Å)	15.808(3)	15.771(3)	11.919(1)	12.8235(7)	10.2771(6)	17.774(2)
c (Å)	23.506(5)	23.410(5)	12.939(1)	14.4284(8)	19.391(1)	16.256(2)
α (°)	85.82(3)	85.57(3)	64.900(3)	101.240(1)	90	90
β (°)	83.63(3)	83.64(3)	73.960(3)	99.721(1)	99.51(1)	95.039(1)
γ (°)	75.20(3)	75.28(3)	64.500(3)	112.983(1)	90	90
V (Å^3)	4219(1)	4193(1)	1310.6(2)	1661.9(2)	3673.6(3)	7503.1(5)
Z	2	2	1	2	4	4
D_{calc} (g cm^{-3})	1.509	1.518	1.667	1.644	1.596	1.436
Crystal size (mm)	0.25 × 0.3 × 0.4	0.25 × 0.3 × 0.4	0.40 × 0.25 × 0.25	0.25 × 0.25 × 0.35	0.25 × 0.3 × 0.3	0.30 × 0.30 × 0.20
μ(Mo Kα) (cm^{-1})	9.11	9.70	15.15	12.87	11.72	11.33
$2\theta_{max}$ (°)	57.0	56.9	52.6	52.6	52.5	54.1
Reflections collected	29 354	29 152	7706	9760	20 061	19 206
Unique reflections	18 610 (R_{int} 0.038)	18 460 (R_{int} 0.042)	5200 (R_{int} 0.016)	6551 (R_{int} 0.017)	7403 (R_{int} 0.022)	7409 (R_{int} 0.035)
Observed reflections	13 219	13 328	3940	4449	5744	5141
Data/parameters	18 454/1035	18 460/1035	4895/308	5898/389	6588/453	7409/379
R_1, wR_2 [$I > 2\sigma(I)$]	0.049, 0.115	0.043, 0.099	0.039, 0.103	0.037, 0.088	0.032, 0.076	0.058, 0.117
R_1, wR_2 (all data)	0.082, 0.145	0.071, 0.108	0.056, 0.111	0.053, 0.113	0.047, 0.095	0.095, 0.139
Goodness-of-fit on F^2	1.068	1.051	1.062	1.085	1.012	1.046
Residual peaks (e Å^{-3})	0.56 − 0.52	0.48 − 0.47	0.58 − 0.47	1.03 − 0.86	0.60 − 0.34	1.40 − 1.00

insoluble in water. All these solvated copper compounds are unstable in air and eventually loose crystallinity.

3.2. Measurements

IR-spectra of the compounds were recorded using an UR-10 spectrometer (Carl Ziess, Jena) in the range 4000–400 cm^{-1} (KBr pellets). Electronic diffuse reflectance and absorption spectra were recorded on a SPECORD M40 (Carl Zeiss, Jena) UV–Vis spectrometer and on a KSVU-23 (LOMO, USSR) IBM PC adapted spectrophotometer, respectively. DTA measurements were made in the temperature range of 20–400 °C using a Q-1500 'Quasi' thermoanalyzer at the heating rate of 2 °C min^{-1}.

3.3. Crystal structure determination

Crystallographic measurements were made using a Siemens SMART CCD area-detector diffractometer (graphite monochromated Mo Kα radiation, $\lambda = 0.71073$ Å, omega scans, $\Delta\omega$ 0.2°, exposition time 30 s per frame, empirical absorption corrections using SADABS [24]). The essential experimental conditions and crystal data are given in Table 4. The structures were solved by direct methods and refined in the anisotropic approximation using SHELXS-86 and SHELXL-93 [25,26]. All the non-hydrogen atoms were refined anisotropically. The hydrogen atoms of ethyl groups and morpholine rings were included in the refinement as fixed contributions with their isotropic U values set invariant at 0.08 Å^2. Structures **3** and **5** show typical rotational disordering of heavy chlorine atoms of CCl_3 groups over two closely related positions with almost equal contributions. Refinement of the disorder model proceeded smoothly and therefore no geometry constraints were employed and disordered atoms were refined anisotropically for the sake of overall convergence. The principal interatomic distances and bond angles are listed in Tables 2 and 3.

Graphical representation of the structures was made using program Diamond [27].

4. Supplementary data

Crystallographic data (excluding structure factors) for the structural analysis have been deposited with the Cambridge Crystallographic Data Centre, CCDC Nos. 197767–197772 for compounds **1**–**6**, respectively. Copies of this information may be obtained free of charge from The Director, CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (fax: +44-1223-336033; e-mail: deposit@ccdc.cam.ac.uk or www: http://www.ccdc.cam.ac.uk).

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