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Metal Dependence of Network Dimensionality in 1,2,4-Diazaphospholide Coordination Polymers

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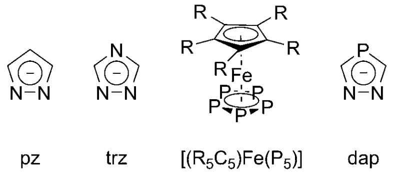
Coordination polymers constructed from metals and bridging organic ligands are currently being intensely explored because they offer interesting physical properties or potential uses (e.g. for ion exchange, adsorption, and catalysis).[1] Although various structural architectures are easily synthesized,[2] control in the assembly of the network topology is still a great challenge. Five-membered heteroaromatics with several Group 15 donor atoms have recently been employed with some success because they offer rigid structures that support directional metal coordination, and a tendency to form polynuclear clusters that can serve as defined building blocks. Examples with polydentate N-donor ligands include pyrazolide (pz) and 1,2,4-triazolide (trz) based coordination polymers with 1D to 3D network topologies,[3,4] and pentaphosphaferrocenes [$(R_5C_5)Fe(P_5)$] have been employed as building blocks to construct P-donor-based 1D and 2D polymeric networks and spherical oligomeric assemblies (Scheme 1).[5]



Scheme 1.

The successful utilization of both P- and N-based homotopic ligands suggested that heterotopic P,N-heterocycles are likewise viable building blocks, in which the presence of two types of donor sites with different ligating power might allow, as an additional advantage, the observation of switchable coordination behavior. In particular, we envisaged that the known preference of the two-coordinate phosphorus to behave as soft donor should allow the ligand to use both P- and N-donor functions to bind to soft metal ions, whereas only N-donor sites should be involved in binding of hard metal ions, thus enabling the construction of coordination polymers with different network topologies from the same ligand. Here, we report on the results of some initial experiments conducted along these lines. The bridging ligand employed, 1,2,4-diazaphospholide (dap),[6] was chosen because its hydrolytic stability offers the prospect of developing the coordination chemistry of low-coordinate phosphorus compounds in aqueous solution, and because 1,2,4-diazaphospholides form molecular complexes with a remarkable variability of bonding modes.[7] Although μ-bridging coordination modes have been established in several of these complexes, it seems, however, that the deliberate synthesis of coordination polymers has not been attempted.

Experiments aimed at the syntheses of 1,2,4-diazaphospholide salts with distinguishable network topologies were performed by reacting aqueous solutions of 1,2,4-diazaphosphole (dapH) with zinc chloride and silver nitrate, respectively. Zinc(II) is known to form a variety of stable complexes with N-donors but lacks a strong affinity for P-donors, whereas silver(I) binds easily to both types of ligands and even has a slight preference for P-coordination. The products precipitated upon mixing of the reactants as colorless, microcrystalline solids that were insoluble in common organic solvents and were characterized by elemental analyses, solid-state ^{31}P and ^{13}C NMR spectroscopy, and powder X-ray diffraction studies. The zinc salt [$Zn(dap)_2$] dissolved in strongly acidic ($pH < 2$) or alkaline ($pH > 13$) aqueous solution but could not be recrystallized from these solutions at intermediate pH. The silver salt [Ag(dap)] was only soluble in concentrated sulfuric acid, and

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crystals suitable for a single-crystal X-ray diffraction study were obtained by careful dilution of this solution.

The first evidence for the presence of different types of metal–ligand interactions in [Ag(dap)] and $[Zn(dap)_2]$ was obtained from solid-state ^{31}P NMR spectra. The zinc salt displays spectral parameters similar to those of the free ligand dapH, and the isotropic chemical shifts δ_{iso} and the individual principal components δ_{ii} of the magnetic shielding tensors of both compounds match within a few ppm (Table 1). As metal coordination at phosphorus is usually accompanied by perceptible chemical shift changes, we conclude that the ligand interacts with the zinc ions exclusively via the N-donor sites. In contrast, [Ag(dap)] displays a decrease in δ_{iso} by some 65 ppm, which is due to marked upfield shifts of the principal components δ_{11} and δ_{22} (Table 1), and results in a distinctly unsymmetrical shielding tensor (with $\delta_{11} \gg \delta_{22} \gg \delta_{33}$) rather than a nearly axial one ($\delta_{11} \approx \delta_{22} \gg \delta_{33}$) as in dapH and $[Zn(dap)_2]$. These changes are clearly identified as coordination shifts arising from direct interaction of the phosphorus atom in [Ag(dap)] with one (or more) metal atoms.[8] Further attempts to elucidate the coordination environment by analysis of coupling patterns between ^{31}P and magnetically active $^{107/109}Ag$ nuclei ($I = 1/2$) in CP-MAS spectra failed, however, as the spectra displayed only broad lines without resolved fine structure.

Table 1. Solid-state ^{31}P NMR data [ppm] of dapH, $[Zn(dap)_2]$, and [Ag(dap)].

	δ_{iso}	δ_{11}	δ_{22}	δ_{33}
dapH	81.4	196	161	−117
$[Zn(dap)_2]$	80.4	183	183	−131
[Ag(dap)]	14.6	166	−8	−116

The conclusions derived from the NMR data were confirmed by X-ray diffraction studies. The zinc salt $[Zn(dap)_2]$ (space group *Ibam*) is isostructural with zinc bis-pyrazolate,[3] $[Zn(pz)_2]$. Each zinc atom is coordinated by four nitrogen atoms that belong to four different anions and forms a nearly tetrahedral coordination sphere with N-Zn-N angles of 105–112°. The Zn−N distances (1.978(5) Å) match those in $[Zn(pz)_2]$ (1.970(7) Å[3]). The nitrogen atoms of each diazaphosphole unit bind to different zinc atoms, whereas the phosphorus atom remains inert, resulting in a μ_2-bridging $\kappa N,\kappa N'$-coordination mode for a single anion (Figure 1 a). The deviation of endocyclic bond lengths (cf. Figure 1) from values in other diazaphospholide complexes (P−C ≈ 1.73 Å, C−N ≈ 1.33 Å, N−N ≈ 1.37 Å[7]) is presumably an artefact of the structure refinement.

The crystal packing in $[Zn(dap)_2]$ is best described as being composed of one-dimensional arrays of zinc ions that are aligned parallel to the crystallographic *c* axis. Adjacent metal ions in each array are linked by two diazaphospholide anions to form planar N_4Zn_2 rings, and adjacent rings are mutually orthogonal to give one-dimensional columnar coordination polymers (Figure 2). The distance between adjacent zinc atoms in a chain is $c/2 = 3.661(1)$ Å, and the closest distance between phosphorus atoms in different hexagonally packed stacks (4.12(2) Å) is only slightly larger than the distances between the 4-carbon atoms in the anions of $[Zn(pz)_2]$[3] so that, on the whole, the formal replacement of a CH unit in $[Zn(pz)_2]$ by a phosphorus atom has only minor structural impact.

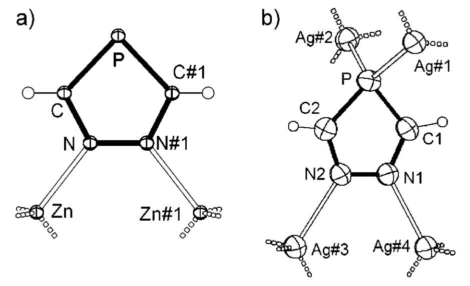

Figure 1. Coordination environment of the anions in $[Zn(dap)_2]$ (a) and [Ag(dap)] (b). Selected distances [Å]: $[Zn(dap)_2]$: Zn−N 1.978(5), C−N 1.354(7), P−C 1.769(6), N−N#1 1.265(13); [Ag(dap)]: P−C1 1.750(5), P−C2 1.757(5), C1−N1 1.320(6), C2−N2 1.318(5), N1−N2 1.375(5), N1−Ag#4 2.262(4), N2−Ag#3 2.274(3), P−Ag#1 2.551(1), P−Ag#2 2.537(1).

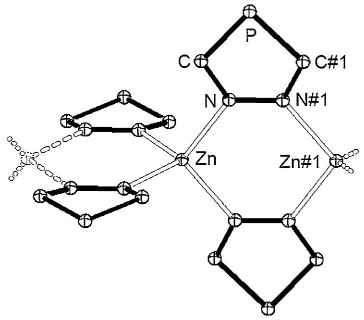

Figure 2. Representation of two repetition units of the one-dimensionally infinite coordination polymers in $[Zn(dap)_2]$.

In contrast to the homoleptic metal environment in $[Zn(dap)_2]$, the silver ions in [Ag(dap)] (space group *Pbca*) are surrounded by two nitrogen and two phosphorus donor atoms that form likewise a distorted tetrahedral coordination sphere. Each anion binds in turn two silver ions via the nitrogen atoms and two more via the phosphorus atom so that the N atoms feature a distorted trigonal planar and the P atom a distorted tetrahedral coordination sphere, respectively (Figure 1 b).

The Ag−N interactions connect two cations and two coplanar μ_2-$\kappa N,\kappa N'$-donating diazaphospholides to dimeric units with slightly puckered Ag_2N_4 rings; similar structural motifs prevail in $[Zn(dap)_2]$, $[\{Li(dme)(dap)\}_2]$,[7] and in 1,2,4-triazolide complexes.[3] The dimers can be considered as secondary building units that are further connected by Ag−P interactions to link all cations and anions in a single three-dimensional network (Figure 3). If the diazaphospholide ring is reduced to its center of gravity, the crystal packing represents a simple AB system with a distorted wurzite structure in which half of the metal atoms are shifted towards the next anion layer. This network topology must be

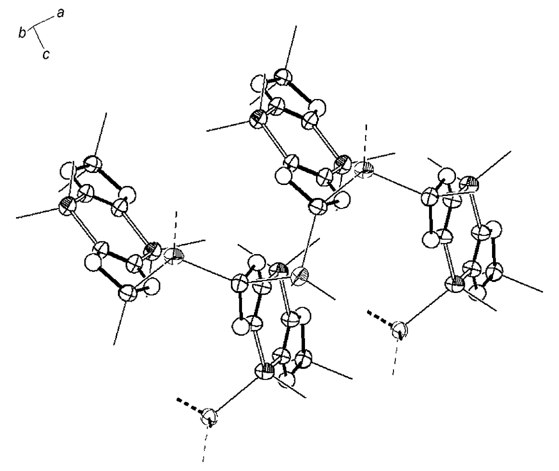

Figure 3. Representation of the crystal packing in [Ag(dap)] showing the assembly of the secondary [$Ag_2(dap)_2$] building blocks to a 3D coordination polymeric network.

considered remarkable when compared with that in complexes of 1,2,4-triazolides such as [Cu(trz)] or [Ag(trz)], in which each donor atom connects with one metal center to form two-dimensional sheetlike assemblies.[3] The capability of a two-coordinate phosphorus atom for μ_2-bridging coordination was previously noted in phospholes[9] or phosphinines[10] and is attributed to the fact that the lone pair exhibits a higher degree of s-character than a lone pair centered at nitrogen, and is thus more diffuse and less directional.[11]

The C–N (1.320(6), 1.318(5) Å) and P–C bonds (1.750(5), 1.757(5) Å) in [Ag(dap)] are indistinguishable from each other and the bond lengths in [{Li(dme)(dap)}$_2$].[7] The P–Ag bonds (2.551(1), 2.537(1) Å) are longer than in tertiary phosphine complexes (Ag–P 2.44 ± 0.07 Å[12]) or in a complex with a μ_2(P)-bound bis-phosphonio-benzophospholide donor (Ag–P 2.37–2.42 Å)[13] but match the distances in disilver complexes with μ_2(P)-bridging phosphole units (Ag–P 2.48–2.86 Å[9]). All findings suggest that the bonding in the Ag_2P unit of [Ag(dap)] should not be described as two electron-precise single bonds like in μ_2(P)-phospholyl complexes, but rather, as in the μ_2(P)-bis-phosphonio-benzophospholide complex,[13] in terms of an electron-deficient three-center bond that involves predominantly the phosphorus lone pair and hardly perturbs the π-electron system of the ligand.

In summary, we have shown that the 1,2,4-diazaphospholide anion supports the construction of coordination polymer networks of different topology by switching between bidentate (κ*N*,κ*N′*) and tridentate coordination; furthermore, the ligand exhibits a remarkable difference to 1,2,4-triazolides because the diffuse lone pair at phosphorus permits μ_2(P)-bridging coordination. Preliminary studies suggest that similar effects are also observable with other metal ions, and that the behavior is predictable in the sense that P-coordination can be suppressed by choosing a metal atom with a low affinity to bind soft phosphorus donor ligands. The results presented serve to stimulate the study of the interaction of the ligand with a wider range of metal ions and, in particular, to include mixed-metal systems, in which selective coordination of individual metals to different donor sites may lead to structural ordering.

Experimental Section

1,2,4-Diazaphosphole was prepared as described by Wilhalm and Schmidpeter.[6]

[Zn(dap)$_2$]: $ZnCl_2$ (390 mg, 2.8 mmol) and dapH (500 mg, 5.8 mmol) were each dissolved in demineralized water (15 mL). Addition of 25% aq. NH_3 (5 mL) to the combined solutions produced a white precipitate that was collected by filtration and dried in vacuum to give the product (440 mg, 64%; m.p. 259 °C. Elemental analysis calcd (%) for $C_4H_4N_4P_2Zn$ (235.43): C 20.41 H 1.71 N 23.80; found C 20.69 H 1.68 N 23.86; IR (Nujol, KBr): $\tilde{\nu} = 1597$, 1343, 1062, 960, 889, 636, 1597 cm^{-1}.

[Ag(dap)]: A solution of $AgNO_3$ (442 mg, 2.6 mmol) in water (10 mL) was added to a solution of dapH (230 mg, 2.6 mmol) in water (10 mL). A colorless precipitate formed almost immediately. The suspension was stirred for 10 min, then the precipitate was collected by filtration and dried in vacuum to give the product (450 mg, 90%; m.p. 143 °C). Elemental analysis calcd (%) for $C_2H_2AgN_2P$ (192.89): C 12.45 H 1.05 N 14.52; found C 12.58 H 0.91 N 14.18; IR (Nujol, KBr): $\tilde{\nu} = 1234$, 982, 869, 838, 830 cm^{-1}. Colorless crystals suitable for single-crystal XRD were obtained by careful dilution of a solution of the solid material in conc. H_2SO_4 with water.

Crystal structure determinations: Crystallographic data of [Ag(dap)] were collected on a Bruker-Nonius Kappa CCD diffractometer at 293(2) K using Mo$_{K\alpha}$ radiation ($\lambda = 0.71073$ Å). Direct Methods (SHELXS-97[14]) were used for structure solution and refinement (SHELXL-97,[15] full-matrix least-squares on F^2). Hydrogen atoms were found in the difference Fourier map and refined free. [Ag(dap)]: colorless crystals, $C_2H_2AgN_2P$, $M = 192.89$, crystal size $0.2 \times 0.2 \times 0.3$ mm, orthorhombic, space group *Pbca* (No. 61), $a = 7.6828(4)$, $b = 11.1218(6)$, $c = 10.6789(6)$ Å, $V = 912.5(1)$ Å^3, $Z = 8$, $\rho(\text{calcd}) = 2.808$ Mg m^{-3}, $F(000) = 720$, $\mu = 4.59$ mm^{-1}, 13741 reflections measured ($2\,\theta_{max} = 56.58°$), 1130 unique ($R_{int} = 0.055$), 64 parameters, 0 restraints, $R1$ ($I > 4\sigma(I)$) $= 0.035$, $wR2$ (all data) $= 0.083$, largest diff. peak and hole 0.61/−0.98 e Å^{-3}, numerical absorption correction (HABITUS).

Crystallographic data of [Zn(dap)$_2$] were collected on a Philips X′Pert MPD powder diffractometer with primary beam Ge monochromator using Cu$_{K\alpha 1}$ radiation. The originally supplied powder was annealed for one day at 250 °C in an evacuated quartz tube and then quenched. This removed a considerable part of anisotropic microstrain broadening along [010], some of which nevertheless remained and had to be considered during the Rietveld refinements. The isostructural character with the corresponding triazolide[3a] made a structure solution unnecessary, thus Rietveld refinement was directly done with TOPAS3[16] software, applying soft constraints to keep the molecular geometry of the ligand reasonable. An X-ray powder diffraction study of [Ag(dap)] (same measurement conditions as for [Zn(dap)$_2$]) confirmed that the powder formed upon precipitation from water exhibits the same structure as the single crystal isolated from H_2SO_4. [Zn(dap)$_2$]: colorless powder, $C_4H_4N_4P_2Zn$, $M = 235.43$, orthorhombic, space group *I*bam (No. 72), $a = 8.1594(1)$, $b = 14.4813(3)$, $c = 7.3226(1)$ Å, $V = 865.23(3)$ Å^3, $Z = 4$. CCDC-753580 ([Zn(dap)$_2$]) and CCDC-753703 ([Ag(dap)]) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

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Keywords: coordination polymers • heterophospholes • N ligands • P ligands

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