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Phenyldiquinolinylarsine as a nitrogen-arsenic-nitrogen pincer ligand

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Abstract: A nitrogen-arsenic-nitrogen (NAN) ligand, phenyldiquinolinylarsine (**pdqa**), was newly synthesized by utilizing diiodophenylarsine as a key precursor. The copper(I) halide (CuX, X = Cl, Br, I) and gold(I) chloride (AuCl) complexes of **pdqa** were synthesized and their structures were analyzed by NMR spectroscopy and X-ray crystallography. [CuX(**pdqa**)] formed pincer complexes, while only the arsenic atom coordinated to the Au(I) ion in [AuCl(**pdqa**)]. Moreover, it was found that steric strain for forming the pincer coordination was relieved around the arsenic atom, which had less directional coordination, when comparing the structure of a Cul complex with bidentate ligand diphenylquinolinylarsine.

Development of novel ligands is a pivotal process for advancement of coordination chemistry. Numerous backbones and elements have been investigated for superior catalysts, luminophores, magnetic materials, redox systems, etc. Pincer ligands are a particularly important class because the pincer-type complexes can offer high stability and unique reactivity as catalysts.^[1,2] Nitrogen, phosphorus, and carbon atoms are typically employed for the three coordination sites. For further diversity of pincer ligands, various elements, e.g., boron^[3] and silicon,^[4] have been introduced so far. Moreover, incorporation of heavy elements is an emerging strategy toward new class of pincer ligands.^[5-7] Germylenes (Figure 1a)^[6] and stannylenes (Figure 1b),^[7] being analogues of carbene, are used for phosphorus-germanium-phosphorus and phosphorus-tinphosphorus pincer ligands, respectively. Such carbene-like species require intramolecular donor-stabilization as represented by N-heterocyclic carbenes. As more simple ligand design, heavy element-containing pincer ligands can be constructed by using group 15 elements such as arsenic, antimony, and bismuth. Among them, arsenic is favorable because arsenic(III) has sufficient stability against inversion, oxidation, and decomposition. In comparison, nitrogen has low inversion barrier to cause racemization at room temperature, phosphorus is easily oxidized to be pentavalent state in air, and molecular design for organoantimony and organobismuth compounds is restricted due to relatively unstable Sb-C and Bi-C bonds.



Figure 1. Representative examples of pincer complexes with heavy elementcontaining ligands: (a) germanium, (b) tin, (c, d) arsenic.

Despite their promise, arsenic-containing pincer ligands have been rarely studied to date. Nishibayashi and coworkers reported an arsenic-nitrogen-arsenic (ANA) pincer ligand as analogues of phosphorus-nitrogen-phosphorus one (Figure the 1c).^[8] Ruthenium complexes with the ANA ligand can work as a catalyst with high selectivity for dehydrogenation transformations.^[8b] On the other hand, arsenic-centered pincer ligands, e.g., nitrogenarsenic-nitrogen (NAN) type, are unexplored. Phosphorus analogues, NPN type, have been employed in coordination chemistry.^[9] For example, a high-spin iron ylide complex is supported by an NPN ligand to proceed alkylidene-transfer reactions. The preceding NPN chemistry has motivated us to explore NAN ligands.^[9e] Although Wild and coworkers synthesized bis(6-methylquinolin-8-yl)phenylarsine and tris(6methylquinolin-8-yl)arsine as multidentate arsenic ligands, the pincer type complexes were not examined.^[10]

The major challenge for the development of NAN ligands lies in a lack of synthetic methods for organoarsenic compounds. Traditional As–C bond formation reactions need volatile and toxic precursors such as arsenic chlorides and hydrides. Serious safety concerns have kept researchers away from experimental studies on organoarsenic-related chemistry. To get over the barrier, we

have developed various synthetic routes towards organoarsenic compounds by utilizing non-volatile arsenic precursors.^[11] The key materials are cyclooligoarsines, which can be prepared from inorganic arsenic compounds.^[12] Cleavage of the As–C bonds generates reactive species, *i.e.*, radicals, electrophiles, and nucleophiles, *in situ*. In particular, diiodoarsines (RAsI₂) have given various kinds of functional organoarsenic compounds; RAsI₂ can be easily prepared by only mixing cyclooligoarsine with iodine (I₂).^[13] In this work, we newly synthesized a NAN ligand, as a novel class of pincer ligands (Figure 1d). The copper(I) halide (CuX, X = CI, Br, I) and gold(I) chloride (AuCI) complexes of **pdqa** were examined to understand the coordination behaviors.

The target NAN ligand **pdqa** was synthesized according to Scheme 1. A tetrahydrofuran (THF) solution of diiodophenylarsine (PhAsl₂) was prepared by our reported protocol.^[13] 8-Bromoquinoline was lithiated by *sec*-butyllithium (*s*-BuLi), and then the THF solution of PhAsl₂ was added to obtain **pdqa**. The chemical structure of **pdqa** was determined by NMR spectroscopy, high resolution mass analysis, and X-ray crystallography.^[14] The solid sample of **pdqa** was quite stable under ambient condition; negligible change was observed in ¹H-NMR even after storage for more than 2 months. This is because the arsenic(III) atom has sufficient oxidative resistance. Hydrogen peroxide (H₂O₂), not oxygen in air, was necessary (for detail, see supporting information).



Scheme 1. Synthesis of NAN ligand pdqa.

The NAN ligand pdga was mixed with CuX (X = Cl, Br, I) and AuCl to produce complexes [CuX(pdga)] (Scheme S1) and [AuCl(pdqa)] (Scheme S2), respectively. NMR spectra were measured for structural analysis of the obtained complexes in solutions. We focused on some of the signals due to the guinolinyl group; the protons at 2-, 4-, 5-, and 7-positions are defined as H(a), H(b), H(c), and H(d) (Figure 2). The changes of the chemical shifts after the coordination were dependent on the metals. This means that coordination forms were different between [CuX(pdqa)] and [AuCl(pdqa)], considering that the electron density of the protons near coordination sites should be lowered to cause downfield shift. The signals due to the pyridine moiety (H(a) and H(b)) of [CuX(pdqa)] were significantly shifted to downfield, while those of the [AuCl(pdqa)] showed negligible shift. On the other hand, the signals due to the benzene ring were shifted to downfield in all the complexes. These results strongly support the idea that the Cu(I) ions coordinated to the arsenic and nitrogen atoms, whereas the Au(I) ion coordinated to only the arsenic atom. Au(I) ion in general prefers coordinate number of two, and soft Lewis basicity of arsenic gave strong interaction between the arsenic atom and gold(I) ion, compared with the quinoline moieties having harder Lewis basicity.



Figure 2. ¹H-NMR spectra (400 MHz in CDCl₃) of bare ligand **pdqa** and complexes [CuX(**pdqa**)] (X = Cl, Br, I) and [AuCl(**pdqa**)]. The protons at 2-, 4-, 5-, and 7-positions of the qunolinyl group are defined as H(a), H(b), H(c), and H(d).

For further study on the structures, the molecular structures were determined by single crystal X-ray diffraction. Single crystals suitable for the analysis were obtained for [CuBr(pdqa)], [Cul(pdqa)], and [AuCl(pdqa)] by recrystallization from CH₂Cl₂/methanol or CH₂Cl₂/hexane at room temperature. Though the result of [CuBr(pdqa)] indicated the presence of two conformations, one conformer is discussed here; there is no significant conformational difference between the two conformers (for the data of the other, see supporting information). Initially, it was confirmed that pdga worked as NAN-pincer and Asmonodentate ligands for Cu(I) and Au(I) ions, respectively. This result well corresponds to the observation for the NMR spectroscopy shown above. The Cu(I) ions of [CuX(pdga)] (X =Br, I) adopted distorted tetrahedral structures in reference to the As-Cu-X, N-Cu-X, N-Cu-As, and N-Cu-X bond angles. The sum of the N-Cu-As and N-Cu-X angles were 402.8° (X = Br) and 393.5° (X = I), which are far from that of a regular tetrahedron (ca 438°). This suggests that the tetrahedral metal centers were planarized by the NAN pincer backbone. On the other hand, the Au(I) ion possessed a linear coordination form considering the As-Au-Cl bond angle (174.60(7)°). In addition, it was found that the As-Cu bond length of [CuBr(pdga)] (2.374(2) Å) was slightly shorter than that of [Cul(pdqa)] (2.403(1) Å). This is probably because the trans-influence of the former is weaker than that of the latter due to the weaker σ -donation of the bromide ion.



Figure 3. ORTEPs (top: top view, bottom: side view) of (a) [CuBr(**pdqa**)], (b) [Cul(**pdqa**)], and (c) [AuCl(**pdqa**)]. C^{Ph}–As–M bond angles are posted (below). Hydrogen atoms were omitted for clarity. Thermal ellipsoids are drawn at the 50% probability level. [CuBr(**pdqa**)] had two conformations, but one conformer displayed here (for the other, see supporting information).

Interestingly, the bond angles around the arsenic atoms were highly distorted in [CuX(pdqa)] compared with those of [AuCl(pdqa)]. The carbon atoms attached to the arsenic atoms are defined as C^{Ph} (phenyl group) and C^{Qu} (quinolinyl group). The conformation of the arsenic atom of [AuCl(pdga)] was a nearly regular tetrahedron because the bond angles around the arsenic atom were 101.6(4)°-120.1(3)°. In contrast, the CPh-As-Cu and C^{Qu}-As-Cu bond angles of [CuX(pdga)] had wide ranges, *i.e.*, $94.8(2)^{\circ}-152.9(2)^{\circ}$ (X = Br) and $93.7(1)^{\circ}-155.9(1)^{\circ}$ (X = I), while the C^{Ph}-As-C^{Qu} and C^{Qu}-As-C^{Qu} ones were close to 109.5°. Particularly, C^{Ph}-As-Cu bond angles were exceptionally large (vide infra); 152.9(2)° and 155.9(1)° for [CuBr(pdqa)] and [Cul(pdqa)], respectively. Actually, in the case of a Cul complex with an NPN pincer ligand, the corresponding C^{Ph}-P-Cu bond angle was reported to be 130.9(1)°.[9f] In addition, it is notable that the C-N-Cu bond angles were approximately 120°, suggesting that the coordination bonds around the nitrogen atoms were not distorted by the pincer coordination. Density functional theory (DFT) calculations were conducted to optimize the full-geometry of [CuBr(pdqa)] and [Cul(pdqa)] (B3LYP/6-31G(d) for C, H, N and SDD for As, Cu, Br, I).^[15] The estimated CPh-As-Cu bond angles were still large ([CuBr(pdqa)]: 151.2° and [Cul(pdqa)]:

Table 1. Selected bond lengths and angles of [CuBr(pdqa)], [Cul(pdqa)], and [AuCl(pdqa)].^[a]

		[CuBr(pdqa)]	[Cul(pdqa)]	[AuCl(pdqa)]
	M-As	2.374(2)	2.403(1)	2.343(1)
Bond length	M-X	2.356(2)	2.530(1)	2.298(3)
[Â]	Cu-N	2.041(5) 2.040(5)	2.056(3) 2.055(3)	
	As-M-X	138.67(4)	143.64(3)	174.60(7)
	N-Cu-As	86.6(2) 86.7(2)	86.1(1) 85.3(1)	- /
	N-Cu-X	115.1(2) 114.4(2)	111.5(1) 110.6(1)	
	N-Cu-N	110.3(2)	118.9(1)	V .
Bond	C ^{Ph} -As-M	152.9(2)	155.9(1)	115.1(3)
angle [°]	C ^{Qu} –As–M	94.8(2) 94.8(2)	95.2(1) 93.7(1)	110.0(3) 120.1(3)
	C ^{Ph} -As-C ^{Qu}	100.0(3) 104.0(3)	101.0(2) 100.1(2)	105.8(4) 102.6(4)
	C ^{Qu} –As– C ^{Qu}	102.1(3)	102.2(2)	101.6(4)
	C-N-Cu	119.8(4) 121.8(4) 122.2(4) 120.7(4)	119.3(3) 123.0(3) 120.0(3) 119.3(3)	-

[a] M = Cu or Au, X = Cl, Br, or l.

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147.7°) even in the optimized structures under vacuum condition, suggesting that the distorted structures are not attributed by molecular packing in the crystalline states. These results mean that the coordination direction of the arsenic atoms was flexibly adjusted to form pincer complex structures. In general, a lone pair at arsenic has a higher degree of s-character when compared to a lone pair at phosphorus, thus less directional orbital overlap leading to coordination is possible with arsenic compounds.^[16] The Wiberg bond indices (WBIs)^[17] of the As-Cu bonds of [CuBr(pdqa)] and [Cul(pdqa)] in the crystals were estimated by natural bond orbital (NBO) analysis using DFT calculations (B3LYP/6-31G(d) for C, H, N and SDD for As, Cu, Br, I). The results (WBI = 0.45 ([CuBr(pdqa)]) and 0.43 ([CuBr(pdqa)])) indecated that the As and Cu had relatively weak orbital overlap, considering the P-Cu bond of the reported NPN pincer complex[9f] had WBI of 0.51. We thus assumed that arsenic atom is beneficial for construction of pincer ligands because it can mitigate structural strains in the resulting complexes.

To understand the structural features of the arsenic-centered pincer coordination, bidentate ligand, diphenylquinolinylarsine (dpga), was synthesized by nucleophilic substitution of 8bromoguinoline with diphenylarsenolithium^[18] (Scheme 2), and then the Cul complex of dpga was prepared (Scheme S3). The X-ray crystallography revealed that the Cul complex formed iodide-bridged dinuclear rhombic structure, and we thus defined it as [Cu₂l₂(dpga)₂] (Figures 4a and 4b). This result indicates that pincer ligand pdga inhibited cluster formation, which are typically constructed for Cul complexes,^[19] by strict encapsulation of the Cu(I) center. We focused on the bond angles around the arsenic atoms (Figures 4c and 4d). The CQu-As-Cu bond angles of [Cu₂l₂(dpqa)₂] were 94.3(2)° and 95.5(2)°, similar to those of [Cul(pdqa)] (95.2(1)° and 93.7(1)°). On the other hand, the C^{Ph}-As-Cu bond angles of [Cu₂l₂(dpqa)₂] (118.9(2)-131.6(2)°) were much smaller than that of [Cul(pdqa)] (155.9(1)°). The large bond angle of [Cul(pdqa)] strongly supports the idea that the distortion attributed to the pincer coordination was concentrated around the arsenic atom, which flexibly mitigated it.



Scheme 2. Synthesis of bidentate ligand dpqa.



Figure 4. (a) Chemical structure and (b) ORTEPs of $[Cu_2l_2(dpqa)_2]$. Hydrogen atoms were omitted for clarity. Thermal ellipsoids are drawn at the 50% probability level. Bonds around arsenic atoms are depicted for (c) [Cu(pdqa)] and (d) $[Cu_2l_2(dpqa)_2]$ based on the results of X-ray crystallography.

In conclusion, we have newly developed NAN-pincer ligand phenyldiquinolinylarsine (**pdqa**). The ligand formed pincer coordination with CuX (X = Cl, Br, I), while only the arsenic atom was selectively interacted to an Au(I) center for AuCl. It is notable that the distortion attributed to the pincer coordination was relieved by the less directional coordination of the arsenic atom. We are now investigating complexes containing **pdqa** and related ligands in catalysis. This new class of pincer ligands, giving unique structures, will contribute to the advancement of coordination chemistry.

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Keywords: arsenic • pincer ligand • copper halide • gold chloride

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In the present work, phenyldiquinolinylarsine has been synthesized as the first example of a nitrogen-arsenic-nitrogen (NAN) pincer ligand. It was demonstrated that copper halide complexes of the NAN ligand formed pincer coordination. Importantly, steric strain attributed to the pincer coordination was relieved by the less directional coordination of the arsenic atom.