A dianionic C\textsubscript{3}-symmetric scorpionate: synthesis and coordination chemistry\textsuperscript{†}

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Introducing charges into ligand systems fine-tunes their electronic properties and influences the solubility of their metal complexes. Herein, we present a synthesis of a dianionic, C\textsubscript{3}-symmetric ligand combining three anionic N-donors tethered to a positively charged phosphonium center. The tris-skatylmethylphosphonium (TSMP) ligand, isolated in the form of its dipotassium salt TSMPK\textsubscript{2}, is the first dianionic homoscorpionate capable of metal exchange. The potassium cations in TSMPK\textsubscript{2} are exchangeable for other metals, which results in rich coordination chemistry. Thus, the ligand displays a bridging \(\kappa^2: \kappa^2: \kappa^3\) coordination mode with trigonal planar Cu(I) centers in the tetrameric complex \([\text{TSMP}]\text{Cu}_4\)\textsuperscript{4+}. The \(\kappa^3\) mode is accessed upon addition of 1 equiv. of P(OEt)\textsubscript{3} per Cu(I) to yield the tetrahedral monomeric complex \([\text{TSMP}]\text{CuP(OEt)}_3\)\textsuperscript{−}. Both Fe(I) and Ni(I) in pyridine give octahedral high-spin \(\kappa^5\) complexes with composition \([\text{TSMP}M\text{Py}_3\) (\(M = \text{Fe, Ni}\)). Displacement of three pyridine ligands in \([\text{TSMP}]\text{Fe(Py)}_3\) for a second equivalent of TSMP gives a high-spin pseudotetrahedral 2 : 1 complex \([\text{TSMP}]\text{Fe}^{2+}\)\textsuperscript{−} with the ligands in \(\kappa^2\) coordination mode. The reduction in coordination number is likely due to electrostatic repulsion of the negatively-charged indolides as well as their weaker \(\pi\)-accepting character as compared to pyridine.

Introduction

The term “scorpionate” was introduced by Trofimenko\textsuperscript{1} and refers to tripodal tridentate ligand systems that are able to coordinate to a metal with two identical donor moieties, similarly to the pincers of a scorpion. The third donor moiety rotates forward akin to a scorpion stinger to attack the metal in a fac manner. If it is identical to the first two, a C\textsubscript{3}-symmetric homoscorpionate complex forms; otherwise, coordination results into a heteroscorpionate complex.

Most scorpionates are six-electron donors, which makes them isoelectronic to another common ligand, cyclopentadienyl (Cp). A considerable amount of research was done to compare these two systems.\textsuperscript{1,2} It is important to point out, however, that while they are isoelectronic, they are not isomeric,\textsuperscript{3} therefore the extent of such a comparison is limited. Additionally, in some situations, scorpionates are capable of displaying a \(\kappa^5\) coordination mode freeing the third arm for binding to another metal center,\textsuperscript{1} which sets them apart from Cp ligands.

The first generation of homoscorpionates involved trispyrazolylborates\textsuperscript{1} and proved to be highly versatile spectator ligands. By modifying the nature, number and position of substituents of the pyrazolyl rings, a wide range of ligands was prepared enabling both electronic and steric properties of a coordinated metal to be fine-tuned. Such systems have found applications in biomimetics,\textsuperscript{4} catalysis,\textsuperscript{5} material science\textsuperscript{6} and production of radiopharmaceuticals.\textsuperscript{7} Following this success, the definition of scorpionates has been extended to tripodal tridentate systems with other donor groups and bridging constituents of the pyrazolyl rings, a wide range of ligands was prepared enabling both electronic and steric properties of a coordinated metal to be fine-tuned. Such systems have found applications in biomimetics,\textsuperscript{4} catalysis,\textsuperscript{5} material science\textsuperscript{6} and production of radiopharmaceuticals.\textsuperscript{7} Following this success, the definition of scorpionates has been extended to tripodal tridentate systems with other donor groups and bridging atoms. Among the employed donors are imidazole,\textsuperscript{8} pyridine,\textsuperscript{9} triazole,\textsuperscript{10} indole,\textsuperscript{11} methimazole,\textsuperscript{12} oxazoline,\textsuperscript{13} N-heterocyclic carbenes\textsuperscript{14} and others, and even acyclic donor groups.\textsuperscript{15} Variation of the bridging atom allowed to further tune electronics and charge of the scorpionate ligands, thus influencing coordination behavior and solubility of their complexes. Reported systems include CH/COH,\textsuperscript{9} CH\textsubscript{3}C\textsubscript{6}H\textsubscript{5}-Si,\textsuperscript{16} N\textsuperscript{9a} P,\textsuperscript{8,9,17} [R-P],\textsuperscript{18} P=O,\textsuperscript{9b,19} As,\textsuperscript{9c} As=O,\textsuperscript{9b} [CH\textsubscript{3}-Al],\textsuperscript{20} [CH\textsubscript{3}-Ga],\textsuperscript{21} C\textsuperscript{−},\textsuperscript{22} Si\textsuperscript{23}, Ge\textsuperscript{−}, Sn\textsuperscript{−},\textsuperscript{24} Pb\textsuperscript{−}.\textsuperscript{20}
A more general way to classify the existing C₃-symmetric scorpionates is by formal charge, which is a combined property of the donor moieties and the bridging atom. Thus, one can differentiate neutral, mono-, di- and trianionic homoscorpionate (Chart 1). Whereas there is a plethora of known neutral⁸,⁹,¹⁴,¹⁶,¹⁷ and monoanionic¹,¹⁰,¹²,¹³,²⁰–²² homoscorpionates as well as some trianionic examples,¹¹ dianionic ligands are rare with only one reported precedent¹⁸ (A in Chart 2). The latter was isolated as a LAICl complex, and its LAIME complex could be methylated at phosphorus to a methylphosphonium derivative. However, strong Al–O bonds would likely preclude the possibility of a subsequent metal exchange and make broader exploration of its coordination chemistry difficult.

Herein, we present the synthesis of a C₃-symmetric dianionic ligand B (Chart 2), isolated as its dipotassium salt 1, which fills the aforementioned gap in the assortment of charged scorpionates available for complexation. Taking advantage of the fact that potassium cations are easily exchangeable for other metal ions, we further delve into its coordination chemistry with Cu(I), Fe(II) and Ni(II) salts.

### Results and discussion

#### Ligand synthesis

The dipotassium salt of tris-(2-skatyl)methylphosphonium (1), further abbreviated as TSMPK₂, was synthesized as depicted in Scheme 1. In the first step, skatole (2) was treated with di-tert-butyl dicarbonate (Boc₂O) in the presence of 4-dimethylaminopyridine (DMAP) to yield the corresponding N-Boc derivative (3). The second position of the indole ring was subsequently lithiated with lithium diisopropylamide (LDA) using N-Boc as a directing group. Without isolation, the lithium salt was quenched with a third of an equivalent of PCl₃ to yield tris-2-(N-Boc-skatyl)phosphine (4). The phosphine was then methylated by treatment with an excess (2.0 equiv.) of methyl iodide to form the corresponding methylphosphonium iodide (5). Attempted methylation with an equimolar amount of methyl iodide instead resulted in the incomplete methylation and partial deprotection of the N-Boc-skatole subunits.

It is worth pointing out that tris-2-(N-Boc-skatyl)methylphosphonium iodide (5) exists in DCM-d₂ solution as a ca. 1.00:0.15 mixture of interchanging tris-exo and bis-exo-mono-endo rotamers (see ESI section S4.1†). Complete deprotection of the isolated methylphosphonium iodide 5 can be achieved in a 1:1 mixture of dichloromethane and trifluoroacetic acid (TFA). The product, 6, was subjected to ion exchange using the chloride form of the anion exchange resin Amberlite® IRA-400, affording a white crystalline solid of tris-(2-skatyl)methylphosphonium chloride (7).

Deprotonation of tris-indole 7 with either KHMDS or KH gives the TSMPK₂ salt (1). A highly pure material (>99% according to NMR) was isolated by crystallization from acetonitrile/diethyl ether. X-ray crystal structure determination confirmed the expected molecular structure with a K : P ratio of 2:1 (Fig. 1).

The K⁺ cations are involved in an extensive network of cation–N and cation–π interactions (η¹ to η⁶). The K–N distances vary between 2.723(4) and 3.425(4) Å, and the K–C distances between 2.995(4) and 3.510(4) Å. With such a large variation of distances it is not possible to derive a clearly defined coordination number. Overall, K⁺ coordination leads to the formation of one-dimensional chains in the [110] direction, which are stacked upon each other in c-direction. This stacking...
is interrupted by the inclusion of acetonitrile solvent molecules between every second layer (see ESI section S3†).

The existence of a free alkaline trianionic-monocationic phosphonium salt is, to our knowledge, unprecedented. Quaternary phosphonium salts are generally incompatible with basic counterions and convert either into ylides, phosphoranes26,27,28 or form charge-transfer complexes followed by complex decomposition manifolds.29 The exceptions, however, feature electronically stabilized bulky anions (e.g. diphenylamide30 and 2,4,6-trimethylphenolate31). We speculate that the stability of 1 is due to the above reasons as well: the anionic indolide nitrogen atoms lose a lot of their nucleophilicity due to being involved in an aromatic π-system, and the phosphonium center is too encumbered to accommodate a fourth indolide in its vicinity. Additionally, the latter would experience electrostatic repulsion from other anionic indolides already present in a molecule.

Coordination chemistry of TSMP

In order to study the ligation behaviour of the novel TSMP platform, we undertook a series of metal exchange reactions with salt 1. It shows rich coordination chemistry with a number of first-row transition metal salts (Scheme 2).

Reacting equimolar amounts of TSMPK₂ salt 1 with cuprous chloride in pyridine led to an orange-red solution, from which yellow crystalline compound 8 was isolated upon freeing from solvent in vacuo and extraction with THF. NMR spectroscopy in acetonitrile-d₃ reveals one predominant species, albeit an oligomer. To elaborate, the ³¹P NMR spectrum (Fig. 2) shows a single quartet consistent with J P,H coupling with a methyl group. In the ¹H NMR spectrum (Fig. 2), there are two singlets in a 2 : 1 ratio corresponding to aromatic methyl groups CH₃ Ar A and CH₃ Ar B. Moreover, multiplets in the aromatic region are present in the same ratio and, according to magnitude gCOSY (see ESI section S4.2†), constitute two distinct spin systems. This implies 2 : 1 inequivalence of indol-
Fig. 2 $^1$H (400 MHz) and $^{31}$P NMR (162 MHz) spectra of 8 in acetonitrile-$d_3$. Lilac arrows in the structural formula indicate diagnostic NOESY correlations discussed in the text. Only one of two equivalent CH$_3^{eta}$ correlations is shown.
analogue \( [[\text{C}(3,5-\text{Me}_2\text{pz})_3]\text{CuP(OMe)}_3]\), which features Cu–N bonds in the range 2.047(2)–2.102(2) Å and a Cu–P bond length of 2.122(2) Å.

Reactions of equimolar amounts of TSMPK2 (1) with either FeCl2 or NiCl2-dme adduct in pyridine give, correspondingly, bright-yellow or olive-brown solutions. Subsequent evaporation of solvent and extraction with THF yield yellow (TSMP)Fe(Py)\(_3\) (10) and green (TSMP)Ni(Py)\(_3\) (11) complexes. All attempts to form related complexes with CoCl2 under the same conditions led to intractable mixtures of products.

According to \(^1\text{H NMR of 10 and 11 in pyridine-}\text{d}_5\), these compounds are paramagnetic, and the number of lines with their integral intensity correspond to three-fold symmetric metallabicyclo[2.2.2]octane topology. Remarkably, in both spectra, the spacing between the pyridine peaks deviates from the normal values by up to 0.3 ppm with \(\alpha\)-pyridine hydrogens being most affected. This difference is likely due to a hyperfine shift induced in pyridine hydrogens upon labile coordination to the metal centers. X-ray structure determination of crystals grown from pyridine/hexane reveals isostructural octahedral complexes that feature one TSMP and three pyridine ligands (10 and 11, respectively, in Fig. 3). Importantly, the FeN\(_6\) core in 10 has much shorter bonds with TSMP nitrogens than pyridine nitrogens, viz. 2.158(6)–2.201(6) Å vs. 2.261(7)–2.351(6) Å (see ESI section S3). In fact, the latter are even longer on average than Fe–N distances in the [FePy\(_6\)]\(^{2+}\) solvate: 2.22(3)–2.29(3) Å. This is consistent with rather weak bonding and the observed lability of pyridine ligands in solution. The NiN\(_6\)
core in 11 shows a similar situation: the Ni–N distances for the TSMP nitrogen atoms are within 2.115(7)–2.148(7) Å, whereas the corresponding values for pyridine nitrogens are 2.163(8)–2.241(8) Å (see ESI section S3†). The long metal–ligand bond lengths in 10 and 11 indicate high-spin electronic states.36 This assignment is also supported by the effective solution magnetic moments measured by Evans method in pyridine-d5: 5.19μB for Fe(n) complex 10 and 2.82μB for Ni(n) complex 11, whereas the spin-only expectation values for S = 2 and S = 1 metal centers, respectively, are 4.90 and 2.82μB.

Interestingly, replacement of three pyridine ligands in 10 with another equivalent of TSMP gives a highly air-sensitive bright-yellow tetracoordinate complex [(TSMP)2Fe]K2, 12a (Scheme 2). The complex can be crystallized from acetonitrile/toluene/ether as the tetrakis(benzo-15-crown-5) adduct 12b (Fig. 3). The NMR spectra of 12a and 12b in solution are identical with the exception of benzo-15-crown-5 peaks. Compound 12b in the crystal features a pseudo-tetrahedral FeN4 core where each TSMP ligand coordinates with two arms while the third remains uncoordinated (κ2 mode). The N–Fe–N angles vary from 96.35(13)° to 119.68(13)° (see ESI section S3†). The angle variance31 of 111.29 deg2 is, consequently, rather large. The distortion is mainly caused by the chelate effect: the dihedral angle between the N11–Fe1–N21 and the N12–Fe1–N22 planes is 85.2(2)° and deviates only slightly from perfect 90°. The Fe–N distances of 2.017(3)–2.028(3) Å indicate a high-spin electronic state of the Fe(n) center. A comparison with structurally related high-spin complexes37 shows similar bonding distances of >2.0 Å. Solution effective magnetic moment measurement by Evans method in pyridine-d5 gives 5.17μB, which is close to the spin-only expectation value of 4.90μB for an S = 2 metal center. The tetrahedral geometry of 12a contrasts with the common octahedral geometry of neutral and dicationic pyrazolate-based bis(scorpionate) Fe(n) complexes38 and of the tris-pyridine complex 10. We speculate that the reduction in coordination number is due to electrostatic repulsion of the negatively-charged indolides as well as their weaker π-accepting properties as compared to pyridine or pyrazolate ligands.

Conclusions

A dianionic C3-symmetric tris-skatylmethylphosphonium (TSMP) ligand platform can be synthesized in the form of dipotassium salt TSMPK2 (1). This system is the first dianionic homoscorpionate capable of metal exchange and fills a gap in the assortment of charged scorpionates. Despite a possibility of recombination between negatively charged indolides and a positively charged phosphonium atom, salt 1 is stable both in the solid state and solution, which is likely due to a combination of electronic and steric factors.

The potassium cations in TSMPK2 (1) are exchangeable for other metals, demonstrating the versatility of TSMP as a ligand for transition metals. The expected scorpionate κ2 binding mode is observed in octahedral, high spin complexes (TSMP)M(Py)2 (10: M = Fe; 11: M = Ni) as well as in the tetrahedral complex [(TSMP)CuP(OEt)3]− (9). In addition, the bridging μ3-κ2:κ1 mode is preferred with Cu(i) in the absence of a co-ligand, affording the tetrameric complex [(TSMP)CuK]4 (8). Finally, the bidentate κ2 mode is observed in the tetracoordinate 2:1 Fe(n) complex [(TSMP)2Fe]2+, which displays a high-spin ground state.

The rich coordination chemistry of the dianionic homoscorpionate ligand invites further investigations. Amongst other, it has a potential to electronically stabilize high-valent metal states due to its electron-rich character, but additional derivatization might be required for kinetic stabilization. Studies in these directions are currently ongoing in our laboratories.

Conflicts of interest

There are no conflicts to declare.

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