Homoleptic Azidometalates

Andreas Kornath*

Azides were discovered by Curtius more than 100 years ago, and even though they are among the most explosive compounds they are still an interesting object of research.[1] It is known that azides of ionic composition, such as those of alkaline and alkaline earth metals do not have a tendency to explode, whereas covalently bonded azides are extremely shock-sensitive compounds.[2] This different behavior is explained by the different bonding situation. In the symmetric azide anion the nitrogen atoms are equally strongly bonded by a double bond. In covalent azides the terminal N–N bond is stronger and thus the exothermic formation of nitrogen inevitable. The driving force is the disproportional increase in the average bond enthalpy for higher bond orders (N–N 159 kJ mol^{-1}; N=N 466 kJ mol^{-1}; N≡N 946 kJ mol^{-1}) which is a fundamental difference between nitrogen and all other elements with the exception of oxygen.

With this in mind it is even more remarkable that recently some very nitrogen-rich, covalent compounds, such as the azidometalates and pentaazonium salts have been reported.[3–6]

Azidometalates have been known for a long time, however there are very few examples of X-ray structure investigations of these salts. The common preparation of azidometalates is based on the reaction of the corresponding chlorometalates with sodium or silver azide. By this method usually not all chloroligands are exchanged for azidoligands. The use of trimethylsiylazide as an azide-transfer agent is an improvement.[3, 4] Recently by this method the synthesis of salts of the ions $[Pt(N_3)_6]^{2-}$ and $[As(N_3)_6]^{-}$ was possible [Eq. (a)].

$$[PPh_4][AsCl_6] + 6\,Me_3SiN_3 \longrightarrow [PPh_4][As(N_3)_6] + 6\,Me_3SiCl \qquad (a)$$

For the stability of the salts formed the choice of the cation plays an important role. Beck et al. found that azidometalates are stabilized by large cations, such as $[PPh_4]^+$ or $[AsPh_4]^+$, and can be handled without danger.[7] Clearly, in the solid state the anions are separated sufficiently, thus a high activation barrier results for the decomposition. However, such a stabilizing effect is not always observed. Dehnicke et al. showed that $[AsPh_4]_2[Pt(N_3)_6]$ follows this rule, but that $[AsPh_4]_2[Pt(N_3)_4]$ with a lower-azide content is shock-sensitive,[4] this arises because the azido groups of the anions are adjacent along one crystallographic axis.

The use of large cations reduces, at least in part, the danger and opens the way for structural investigation of these compounds which are otherwise difficult to handle. ^{14}N NMR spectroscopy of the dissolved salts indicates that the azide groups are covalently bonded to the central atom. The same conclusion can be derived from vibrational spectroscopy of the solid salts which shows that both the symmetrical and antisymmetrical vibrations are visible in the Raman and infrared spectra. The possibility of growing single crystals opens a way to elucidate the variety of azidometalate structures.

A number of anions with up to six azido groups is known from X-ray diffraction studies. The simplest example is hydrogendiazide ($[H(N_3)_2]^-$) with an asymmetric and nearly linear N-H···N bridge. The azido groups are arranged with an dihedral angle of 66°.[8] The ions $[Ag(N_3)_2]^-$ and $[I(N_3)_2]^-$ have the expected C_2 symmetry.[9] In anions with more than two azido groups the central atom has a square planar ($[Pt(N_3)_4]^{2-}$,[4] $[Cu(N_3)_4]^{2-}$,[10] $[Pd(N_3)_4]^{2-}$,[11] $[Au(N_3)_4]^{2-}$[12]), tetrahedral ($[Zn(N_3)_4]^{2-}$,[13] $[Mn(N_3)_4]^{2-}$[14]), trigonal bipyramidal ($[Fe(N_3)_5]^{2-}$),[15] or octahedral ($[Sn(N_3)_6]^{2-}$,[16] $[Pb(N_3)_6]^{2-}$,[17] $[Pt(N_3)_6]^{2-}$,[4] $[As(N_3)_6]^{2-}$,[3] $[Ge(N_3)_6]^{2-}$[5]) coordination geometry with covalently bonded azido ligands which have a bent arrangement around the central atom (Figure 1). The symmetries deviate only slightly from the ideal values.

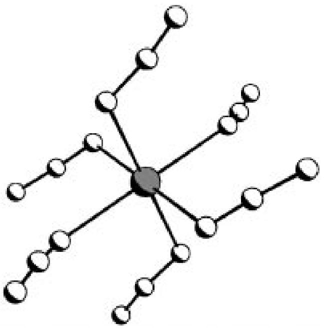
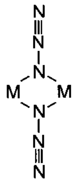


Figure 1. Structure of hexaazidometalates.

Azide groups can act as bridging ligands between metal atoms leading to di- and polynuclear complexes. Two types of connection via azido bridges are known from the chemistry of transition metal azides: type 1 and 2.



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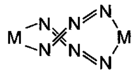

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Only a few examples of dinuclear azidometalates are described in the literature. In the ions $[Fe_2(N_3)_{10}]^{4-}$,[18] $[Pd_2(N_3)_6]^{2-}$,[19] and $[Cu_2(N_3)_6]^{2-}$[20] only azido bridging of type 1 is found (Figure 2). In contrast to the metal azides, the dinuclear anions are stable in solutions. The same type of azido bridging is observed for the infinite-chain polynuclear azidometalate ions $\{[Cd(N_3)_3]^-\}_\infty$, $\{[Cd(N_3)_4]^{2-}\}_\infty$, and $\{[Cd_3(N_3)_{14}]^{8-}\}_\infty$.[21] In contrast the chain structure of the ion $\{[Cu(N_3)_3]^-\}_\infty$ additionally contains an azido bridging of type 2.[22] The $\{[Co_3(N_3)_8]^{2-}\}_\infty$ ion consists of condensed units

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[*] Priv.-Doz. Dr. A. Kornath
Fachbereich Chemie der Universität
44221 Dortmund (Germany)
Fax: (+49) 231-7553837
E-mail: kornath@citrin.chemie.uni-dortmund.de

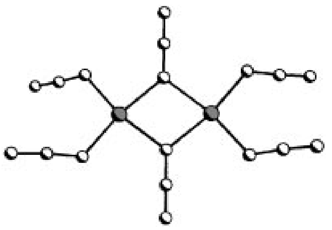

Figure 2. Structure of a dinuclear azidometalate ion; $[Cu_2(N_3)_6{}^{2-}]$.

of type 1 arranged in infinite chains that are connected by 1,3-azido bridge (half type 2) forming infinite layers.[23] An example for three-dimensional bridging is given by the $\{[Mn(N_3)_3]^-\}_\infty$ ion, that possesses a perovskite-like structure with a 1,3-azido bridge (half type 2) between the Mn atoms.[22]

From the relatively few examples of homoleptic azidometalates one can assume that a large variety of structures is possible. Moreover the azidometalates are interesting for material science because of their magnetic properties. It is known that azido bridging of type 1 leads to a ferromagnetic coupling whereas type 2 results in an antiferromagnetic coupling. In some cases cooperative magnetic long-range effects are observed (molecular magnets).[24]

Large cations and improved syntheses, for example, by making use of trimethylsilylazide could facilitate access to new azidometalates. Transferring the stabilizing effect to cationic species by employing large counter anions is also conceivable; recently $[N_5{}^+][AsF_6{}^-]$ has been prepared by K. O. Christe et al. (Figure 3).[6] In contrast to the azidometalates, the bent pentaazonium cation is mesomeric stabilized thus no isolated single N–N bonds are present. Both, the increase of stability gained by using larger anions and the preparation of such an unusual salt as $[N_5{}^+][N_3{}^-]$ seem feasible, however, one should consider that this hypothetical new modification of nitrogen is a combination of an oxidizing cation and a reductive anion. The examples show that surprising results can be expected from the azide chemistry in near future.

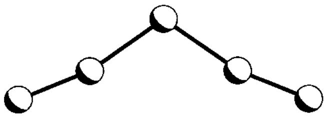

Figure 3. Structure of the pentaazonium cation $[N_5]^+$.

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