

Bis(triphenylphosphoranylidene)ammonium Dicyanoaurate(I)

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Di(cyano)aurates(I), Gold(I) Cyanide Complexes, Bis(triphenylphosphoranylidene)ammonium Salts

Partially ^{13}C -labeled alkali dicyanoaurates $\text{M}[\text{Au}(\text{CN})_2]$ were prepared and investigated by NMR and IR spectroscopy in aqueous solution. For the range of concentration investigated the data obtained under standard conditions provided no evidence for anion association. The salt $[\text{Ph}_3\text{PNPPH}_3][\text{Au}(\text{CN})_2]$ was also prepared and the crystal structure of the dichloromethane solvate determined. There is no anion aggregation in the crystal, and short contacts of the anions are only discernible with the solvent molecules. A literature survey of crystal structure data for dicyanoaurate(I) salts (almost 35 entries) show that inter-anionic contacts are only observed in structures with small cations or with cations exerting a directional influence.

Alkali di(cyano)aurate(I) salts are the key intermediates in the recovery and processing of gold. Oxidative gold extraction from ores with aqueous alkali cyanide (NaCN or KCN) is followed by adsorption of the produced complexes $\text{Na}[\text{Au}(\text{CN})_2]$ or $\text{K}[\text{Au}(\text{CN})_2]$ on the surface of carbonaceous or resinous materials, for which the linear five-atomic anions $[\text{NC-Au-CN}]^-$ appear to exhibit a specific affinity [1, 2]. Although the details of this adsorption and desorption processes are still not perfectly understood on the molecular level, there is convincing evidence for anion aggregation both in solution, on the substrate surfaces, and in salts with small cations [3 - 5]. During our own investigations [6 - 8] in the supramolecular chemistry of neutral $[\text{L-Au-X}]$, cationic $[\text{L-Au-L}]^+$ or anionic gold(I) complexes $[\text{X-Au-X}]^-$ we noticed that anion aggregation to give oligomers or one-dimensional arrays is observed only in very special cases, and this is also true for the di(cyano)aurate(I) anion [9].

With few exceptions [10, 11], most structural studies were carried out for compounds featuring the rod-like $[\text{Au}(\text{CN})_2]^-$ anion highly oriented between stacks of flat, plate-like cations [9b, 12 - 24]. For several years these materials have been of considerable interest owing to their electrical conductor or semi-conductor properties.

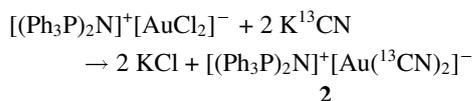
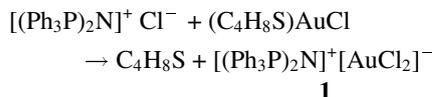
In the present study we tried to prepare and isolate a di(cyano)aurate(I) salt with a very bulky “inno-

cent” cation with high flexibility and no directional influence to allow a spectroscopic and structural characterization of anion association through aurophilic d^{10} - d^{10} interactions in an unperturbing environment both in solution and in the solid state.

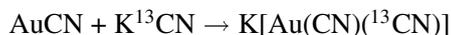
For precise NMR measurements, ^{13}C -enriched cyanide was used in the preparations. ^{13}C -labeled gold pseudohalides were investigated in the course of several earlier studies which provided fundamental data [25, 26]. Previous spectroscopic and structural studies of simple di(cyano)aurates(I) are also summarized in the comprehensive Gmelin Handbook compilation [4].

Preparative and Spectroscopic Studies

For the present investigation, the bis(triphenylphosphoranylidene)ammonium cation [PPN] was chosen as the bulky and highly flexible counterion for $[\text{Au}(\text{CN})_2]^-$. Treatment of (tetrahydrothiophene)gold(I) chloride with an equimolar quantity of $[\text{PPN}]^+\text{Cl}^-$ afforded high yields (84%) of the corresponding di(chloro)aurate(I) (**1**) [27, 28]. This product could be readily converted into the di(cyano)aurate(I) (**2**) by reacting it with two equivalents of KCN in a dichloromethane / water two-phase system. $[\text{PPN}]^+[\text{Au}(\text{CN})_2]^-$ (**2**) was obtained in 87% yield as a colourless crystalline product. Compound **2** was also prepared with ^{13}C -labeled cyanide (99% enriched):



For comparative purposes, ^{13}C -labeled $\text{K}[\text{Au}(\text{CN})_2]$ was prepared (in 89% yield) from unlabeled AuCN and K^{13}CN (99% enriched) to give a product which was approximately 50% enriched in ^{13}C :



For this product, ligand scrambling of labeled and unlabeled cyanide leads to a statistical mixture of three complex anions: $[\text{Au}(^{12}\text{CN})_2]^-$, $[\text{Au}(^{12}\text{CN})(^{13}\text{CN})]^-$ and $[\text{Au}(^{13}\text{CN})_2]^-$.

Spectroscopic Studies

In an attempt to detect anion association equilibria in water, the complexes were investigated by solution infrared and NMR spectroscopy.

Aqueous solutions (*ca.* 3 molar) of K^{12}CN and K^{13}CN show $\nu(\text{CN})$ stretching frequencies at 2078.6 and 2035 cm^{-1} , respectively. Upon complexation to gold(I) in $[\text{Au}(\text{CN})_2]^-$, these bands are shifted and split into bands with maxima at 2145.2 / 2105.0 and 2076.9 / 2034.2 cm^{-1} , respectively. The concentration dependence (between 0.35 and 6.53 molar solutions) is very small and within the standard deviations of the experiment ($\pm 1 \text{ cm}^{-1}$). The corresponding data for complex **2** (in dichloromethane) are 2140.1 / 2098.3 cm^{-1} , again with no significant concentration dependence at ambient temperature.

The ^{13}C NMR resonance of aqueous KCN and $\text{K}[\text{Au}(\text{CN})_2]$ is known to appear at 164.6 and 154.2 ppm [25], respectively. The ^1H , ^{13}C and ^{31}P NMR spectra of compound **2** in CD_2Cl_2 show the multiplets of the phenyl protons/carbons in the range 7.2 - 7.6 / 126.9 - 132.6 ppm and the phosphorus signal as a singlet at 22.3 ppm for the cation. The ^{13}C resonance of the anion appears at 151.3 ppm and is neither concentration nor temperature dependent to any significant extent: For concentrations between 0.040 and 0.200 mol/l the shift displacement is only 0.15 ppm, and for the temperature range 170 - 300 K only 0.2 ppm.

It therefore appears that – using standard equipment – neither vibrational nor NMR spectroscopy are sensitive enough to detect any small effects that could be attributed to aggregation of $[\text{Au}(\text{CN})_2]^-$ anions in solution. By contrast, through UV/Vis absorption and luminescence measurements [5] it was possible to obtain for the first time data on the formation constants of anion dimers in aqueous and methanol solutions of $\text{K}[\text{Au}(\text{CN})_2]$. UV/vis spectroscopy is clearly more sensitive to even small changes in the environment of the cyanoaurate anions as e.g. caused by metal-metal contacts.

This result prompted studies of the crystal structure of the $[\text{PPN}]^+[\text{Au}(\text{CN})_2]^-$ salt, because the large and highly flexible $[\text{PPN}]^+$ cations should provide enough space for the anions to aggregate if the energy associated with the oligomerisation is high enough to compensate deficits in Coulomb energy of cation/anion contacts or other weak packing forces.

Crystal Structure Determination

Crystals of $[\text{PPN}]^+[\text{Au}(\text{CN})_2]^- (\text{CH}_2\text{Cl}_2)_{0.5}$ (from dichloromethane at $-20 \text{ }^\circ\text{C}$) are monoclinic, space group $P2_1/n$, with $Z = 4$ formula units and two molecules of dichloromethane in the unit cell. Cations and anions are well separated and show no sub-van-der-Waals contacts. The cation has a structure which agrees well with the plethora of literature data for salts with the $[\text{PPN}]^+$ unit [29]. The P-N distances of 1.519(3) and 1.584(3) Å and the P-N-P angle of $136.3(2)^\circ$ are comparable to the data found for $[\text{PPN}]^+(\text{BF}_4)^-(\text{CH}_2\text{Cl}_2)$: 1.579(2) / 1.583(2) Å, $138.5(1)^\circ$.

This $[\text{PPN}]^+$ salt with the “innocent” $(\text{BF}_4)^-$ anion and the same interstitial solvent (CH_2Cl_2) was prepared and investigated in this work to have a suitable reference material. The crystals are triclinic, space group $P1$ with $Z = 2$ formula units and two dichloromethane molecules in the unit cell. For details see Experimental Section.

The results show that the $[\text{Au}(\text{CN})_2]^-$ has no specific influence on the structure of the cation, which is known to be very flexible and hence “sensitive” to the presence of sterically unusual or functional anions.

The $[\text{NC-Au-CN}]^-$ anion has no crystallographically imposed symmetry, but its axis of five atoms is almost linear with N-C-Au angles of 178.4(5)

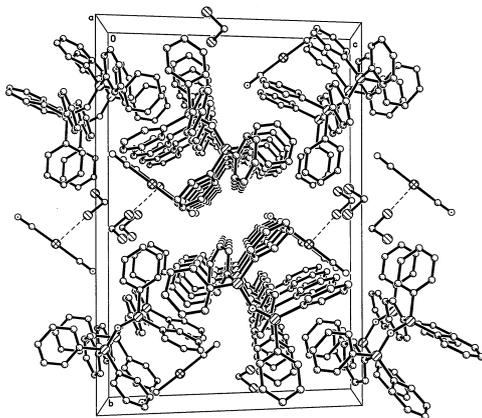


Fig. 1. Projection of the unit cell of $[\text{Ph}_3\text{PNPPh}_3]^+[\text{Au}(\text{CN})_2]^- \times 0.5 \text{CH}_2\text{Cl}_2$ (**2**) onto the bc -plane showing the stacking of the cations and the contacts of the anions and the solvent molecules.

/ 178.7(6) and a C-Au-C angle of $179.1(2)^\circ$. The Au-C distances are similar at 1.929(6) and 1.937(5) Å, as are the C-N distances at 1.084(7) and 1.089(6) Å. The data suggest a completely unperturbed anion geometry which approaches very closely the maximum attainable symmetry of point group $D_{\infty h}$.

There is no evidence for interionic association. The crystal structure of $[\text{PPN}]^+[\text{Au}(\text{CN})_2]^-$ is closely related to that of the dichloroaurate(I) salt $[\text{PPN}]^+[\text{AuCl}_2]^- (\text{CH}_2\text{Cl}_2)$ the crystals of which have very similar cell constants and the same space group. The $[\text{AuCl}_2]^-$ anions also exhibit no tendency to aggregate in the crystal lattice [27, 28]. However, in the crystals of $[\text{PPN}]^+[\text{Au}(\text{CN})_2]^-$ there is a Cl- -Au contact between anions and solvent molecules which may compete (Fig. 1) and be preferred over anion-anion interactions. No solvate-free crystals could be obtained to rule out this alternative.

The present study has demonstrated that anion association in aqueous solutions of $M[\text{Au}(\text{CN})_2]$ salts is very weak and not manifested in concentration-dependent IR and NMR spectra with standard resolution. The anions are also not associated in a crystal where very large and flexible $[\text{PPN}]^+$ cations could give room for oligomerization.

From very detailed theoretical and luminescence studies Patterson *et al.* [5] have estimated the free energy of dimerization (through Au- -Au contacts) to give dianions $\{[\text{Au}(\text{CN})_2]_2\}^{2-}$ as less than -2 kcal/mol (for the potassium salt in aqueous solu-

tion at room temperature). This small gain in energy is obviously not enough to induce rearrangements in an ionic structure against Coulomb forces, and to detect significant changes in NMR chemical shift $[\delta(\text{CN})]$ or vibrational frequencies of strong covalent bonds $[\nu(\text{CN})]$.

In summary the present work has shown that aurophilic interactions between anions $[\text{Au}(\text{CN})_2]^-$ can be maintained only in structures where there is additional support from contacts with counterions or interstitial solvent molecules. Coordinative or hydrogen bonds provide an ideal combination as demonstrated in several previous studies [7, 9]. Bulky substituents with the cationic centers shielded by organic groups as in $[\text{Ph}_3\text{PNPPh}_3]^+$ do not provide such support and therefore the anions remain separated with a preference for contacts to solvate molecules (**2**).

Experimental Section

All experiments were carried out under dry nitrogen. Solvents were dried and saturated with nitrogen, glassware was oven-dried and filled with nitrogen. Standard equipment was used throughout. (Tetrahydrothiophene)gold(I) chloride $[(\text{tht})\text{AuCl}]$ was prepared following a literature procedure [30].

Bis(triphenylphosphoranylidene)ammonium dichloroaurate(I) (**1**) was prepared from $(\text{tht})\text{AuCl}$ (0.560 g, 1.72 mmol) and $[\text{PPN}]\text{Cl}$ (0.998 g, 1.72 mmol) in 30 ml of dichloromethane as described in the literature [27, 28]; yield 1.18 g (84%).

Bis(triphenylphosphoranylidene)ammonium dicyanoaurate(I) (**2**). A solution of $[\text{PPN}][\text{AuCl}_2]$ (0.620 g, 0.696 mmol) in 10 ml of dichloromethane was treated with an aqueous solution (10 ml) of K^{13}CN (0.104 g, 1.57 mmol) for 4 h at room temperature with vigorous stirring. The organic phase was separated and washed twice with 5 ml of dichloromethane. The combined organic phases were washed twice with 5 ml of water and dried over MgSO_4 . The product remained after evaporation of the solvent in a vacuum, yield 0.47 g (87%). - $^{13}\text{C}_2^{12}\text{C}_{36}\text{H}_{30}\text{AuN}_3\text{P}_2$ (789.58): calcd. C 58.06, H 3.73, N 5.32; found C 57.98, H 3.76, N 5.15.

Bis(triphenylphosphoranylidene)ammonium tetrafluoroborate

This compound was obtained from the reaction of equimolar quantities of bis(triphenylphosphoranylidene)ammonium chloride and silver tetrafluoroborate in dichloromethane in virtually quantitative yield. After filtration the product was isolated from the filtrate by evap-

oration of all volatiles. The product shows the PPN cation as the parent peak in the mass spectrum (FAB, $m/e = 538.3$). The $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum (in CD_2Cl_2 at 20°C) has the cation resonance at $\delta = 22.40$ ppm. Single crystals of the dichloromethane solvate (1:1) were obtained from dichloromethane solution upon layering with pentane at -20°C .

Crystal structure determinations

The crystalline samples were placed in inert oil, mounted on a glass pin, and transferred to the cold gas stream of the diffractometer. Crystal data were collected using a Nonius DIP2020 and an Enraf Nonius CAD4 system, respectively, with monochromated Mo- $\text{K}\alpha$ ($\lambda = 0.71073$ Å) radiation at -130°C . The structures were solved by direct methods (SHELXS-97) and refined by full matrix least-squares calculations on F^2 (SHELXL-97). Non-hydrogen atoms were refined with anisotropic displacement parameters. Hydrogen atoms were placed in idealized positions and refined using a riding model with fixed isotropic contributions. The occupation of the solvent molecule CH_2Cl_2 in the crystals of **2** was reduced to 0.5 due to the very large atomic displacement parameters. Complete lists of displacement parameters and tables of

interatomic distances and angles have been deposited with the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK. The data are available on request on quoting CCDS-192015 (1) and 192016 (2).

Crystal data for $\text{C}_{38.5}\text{H}_{31}\text{AuClN}_3\text{P}_2$: $M = 830.02$, monoclinic, $a = 9.1488(1)$, $b = 24.1213(3)$, $c = 16.8338(2)$ Å, $\beta = 105.034(1)^\circ$, space group $P2_1/n$, $Z = 4$, $V = 3587.8(1)$ Å³, $\mu(\text{Mo-K}\alpha) = 42.94$ cm⁻¹, 88429 measured and 7762 unique reflections [$R = 0.055$], $wR2 = 0.1079$, $R = 0.0407$ for 7762 reflections [$I \geq 2\sigma(I)$] and 424 parameters. The function minimized was: $wR2 = \{[\sum w(F_o^2 - F_c^2)^2]/\sum [w(F_o^2)^2]\}^{1/2}$; $w = 1/[\sigma^2(F_o^2) + (ap)^2 + bp]$; $p = (F_o^2 + 2F_c^2)/3$; $a = 0.0466$, $b = 0.98$.

Crystal data for $\text{C}_{37}\text{H}_{32}\text{BCl}_2\text{F}_4\text{NP}_2$: $M = 710.29$, triclinic, $a = 9.495(2)$, $b = 10.635(4)$, $c = 17.020(2)$ Å, $\alpha = 90.28(2)$, $\beta = 94.59(1)$, $\gamma = 93.50(2)^\circ$, space group $P1$, $Z = 2$, $V = 1709.9(8)$ Å³, $\mu(\text{Mo-K}\alpha) = 3.34$ cm⁻¹, 7384 measured and unique reflections, $wR2 = 0.0984$, $R = 0.0465$ for 7384 reflections [$I \geq 2\sigma(I)$] and 424 parameters; weighting scheme: $a = 0.0641$, $b = 0.00$.

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