Synthesis, crystal structure and electrospray ionisation mass spectrometry of a novel one-dimensional cyano-bridged Ni(II)–Au(I) polymer†

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Reaction of nickel(II) acetate with tren [tren = tris(2-aminoethyl)amine] and K[Au(CN)$_2$] produced [Ni(tren)Au(CN)$_2$][Au(CN)$_2$] (**1**), which consists of *cis*-[Ni(tren)]$^{2+}$ units linked by Au(CN)$_2{}^-$ to form infinite zig-zag chains. The complex obeys the Curie–Weiss law throughout the temperature range 4–300 K, with a Curie constant of 1.10 cm^3 K mol^{-1} and a Weiss temperature, θ, of 0.62 K. The electrospray mass spectrum of **1** in H$_2$O–CH$_3$OH shows peaks that can be described by the general formulae $\{[\mathrm{Ni(tren)}]_n[\mathrm{Au(CN)_2}]_{2n-1}\}^+$ (n = 1–4) and $\{[\mathrm{Ni(tren)}]_n[\mathrm{Au(CN)_2}]_{2n-2}\}^{2+}$ (n = 2–9). Based on the crystal structure of the polymer, these ions are best described as composed of an oligomeric cation that may be associated with one or more Au(CN)$_2{}^-$ counter ions.

The chemistry of cyano-bridged polymers is of current interest due to the remarkable diversity of structural types that may be obtained from these systems.[1] A popular approach to the synthesis of these materials has been to use [M(CN)$_6$]$^{n-}$ building blocks in conjunction with a transition metal ion complex, and these have resulted in a number of two-dimensional and three-dimensional polymers. For example, [Ni(en)$_2$]$_3$[Fe^{III}(CN)$_6$]$_2$ · 2H$_2$O (en = ethylenediamine) has a rope-ladder structure;[2] [Ni(1,1-dmen)$_2$]$_2$[Fe^{III}(CN)$_6$]CF$_3$SO$_3$ · 2H$_2$O (1,1-dmen = 1,1-dimethylethylenediamine) has a two-dimensional square structure;[3] [Ni(cyclam)]$_3$-[Cr^{III}(CN)$_6$]$_2$ · 5H$_2$O (cyclam = 1,4,8,11-tetraazacyclotetradecane) has an infinite star-like layered structure;[4] while [Ni(tren)]$_3$[Fe^{III}(CN)$_6$]$_2$ [tren = tris(2-aminoethyl)amine][5] and [Ni(L)$_2$]$_3$[Fe^{II}(CN)$_6$]X$_2$ (L = ethylenediamine or trimethylethylenediamine, X = PF$_6{}^-$ or ClO$_4{}^-$)[6] have three-dimensional network structures. There are, however, no reports on the use of Au(CN)$_2{}^-$ as a bridging ligand for the construction of polymeric metal complexes, although a number of Cd(II) polymers linked by Ag(CN)$_2{}^-$ are known.[7,8] Like CN$^-$, the bidentate, linear nature of Au(CN)$_2{}^-$ is expected to give rise to 1-, 2- and 3-dimensional polymeric materials. The Au(CN)$_2{}^-$ unit, however, has a length of *ca.* 6.2 Å, which is much longer than that of CN$^-$ (*ca.* 1.1 Å); hence it is expected to produce structures very different from those of CN$^-$. We report here the synthesis and structure of [Ni(tren)Au(CN)$_2$][Au(CN)$_2$] (**1**), a novel one-dimensional polymer consisting of bulky *cis*-[Ni(tren)]$^{2+}$ units bridged by Au(CN)$_2{}^-$. The electrospray ionisation mass spectrometry (ESI-MS) of **1** in H$_2$O–CH$_3$OH has also been investigated.

Experimental

Materials

Tris(2-aminoethyl)amine and potassium dicyanoaurate(I) were obtained from Aldrich (St Louis, Missouri). All other chemicals were of reagent grade.

Synthesis of [Ni(tren)Au(CN)$_2$][Au(CN)$_2$] (1). Tris(2-aminoethyl)amine (0.06 g, 0.4 mmol) was added to a solution of Ni(CH$_3$CO$_2$)$_2$ · 4H$_2$O (0.1 g, 0.4 mmol) in water (80 ml), and the mixture was stirred at room temperature for 5 min. A solution of K[Au(CN)$_2$] (0.12 g, 0.4 mmol) in water (30 ml) was then added. The resulting light-purple precipitate was filtered off and dissolved in 1 : 1 MeOH–H$_2$O (*ca.* 150 mL) at approximately 60 °C. Slow evaporation of the solution gave pale purple crystals, which were washed with ethanol followed by ether. Yield: 78%. Anal. Calc. for C$_{10}$H$_{18}$N$_8$Au$_2$Ni: C, 17.08, H, 2.58, N, 15.94. Found: C, 17.30, H, 2.60, N, 15.86%. IR(KBr): ν_{CN} 2144, 2179 cm^{-1}.

Measurements

Infrared spectra were recorded from KBr pellets on a Bomen MB-120 FTIR spectrophotometer.

Variable-temperature magnetic susceptibility measurements were performed on powder samples in the temperature range 4–300 K with a SQUID Quantum Design MPMS-7 magnetometer. Susceptibilities were corrected for diamagnetism using Pascal's constants.

Electrospray ionisation mass spectrometry experiments were performed on a PE SCIEX API 3000 triple quadrupole mass spectrometer (Concord, Ontario) with an *m*/*z* upper limit of 3000 Th. Samples were dissolved in methanol–water (1 : 1)

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† *Non-SI units employed*: 1 Torr ≈ 133 Pa; 1 eV ≈ 9.65 J mol^{-1}.

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Table 1 Crystal data and structure refinement for [Ni(tren)Au(CN)$_2$][Au(CN)$_2$] (**1**)

Empirical formula	$Au_2NiN_8C_{10}H_{18}$
Formula weight	702.94
Crystal system	Monoclinic
Space group	$P2_1/n$ (no. 14)
a/Å	8.140(1)
b/Å	16.191(1)
c/Å	14.008(2)
β/°	105.90(2)
U/Å^3	1775.5(4)
Z	4
T/K	298
μ/cm^{-1}	175.97
F(000)	1280
Measured/independent reflections	3149/1836
R, R_W (%)	0.057, 0.067

Table 2 Selected bond lengths (Å) and angles (°) for **1**

Au(1)–C(7)	1.98(2)	Au(1)–C(8)	1.99(2)
Au(2)–C(9)	1.98(2)	Au(3)–C(10)	1.98(2)
Ni(1)–N(1)	2.09(1)	Ni(1)–N(2)	2.11(2)
Ni(1)–N(3)	2.14(1)	Ni(1)–N(4)	2.09(1)
Ni(1)–N(5)	2.12(1)	Ni(1)–N(6)	2.05(2)
N(5)–C(7)	1.13(2)	N(6)–C(8)	1.13(2)
N(7)–C(9)	1.15(2)	N(8)–C(10)	1.12(2)
C(7)–Au(1)–C(8)	179.5(7)	C(9)–Au(2)–C(9*)	180.0
C(10)–Au(3)–C(10*)	180.0	N(1)–Ni(1)–N(2)	93.4(5)
N(1)–Ni(1)–N(3)	162.8(6)	N(1)–Ni(1)–N(4)	82.9(5)
N(1)–Ni(1)–N(5)	87.6(5)	N(1)–Ni(1)–N(6)	96.5(6)
N(2)–Ni(1)–N(3)	93.3(6)	N(2)–Ni(1)–N(4)	96.5(6)
N(2)–Ni(1)–N(5)	177.0(6)	N(2)–Ni(1)–N(6)	90.0(6)
N(3)–Ni(1)–N(4)	82.1(5)	N(3)–Ni(1)–N(5)	85.0(5)
N(3)–Ni(1)–N(6)	99.2(6)	N(4)–Ni(1)–N(5)	93.3(6)
N(4)–Ni(1)–N(6)	174.0(6)	N(5)–Ni(1)–N(6)	92.6(5)
Ni(1)–N(1)–C(1)	111.0(10)	Ni(1)–N(2)–C(4)	107(1)
Ni(1)–N(3)–C(6)	110.3(10)	Ni(1)–N(4)–C(2)	105.0(10)
Ni(1)–N(4)–C(3)	109(1)	Ni(1)–N(4)–C(5)	106.5(9)
Ni(1)–N(5)–C(7)	175(1)	Ni(1)–N(6)–C(8)	169(1)
Au(1)–C(7)–N(5)	175(1)	Au(1)–C(8)–N(6)	178(1)
Au(2)–C(9)–N(7)	178(1)	Au(3)–C(10)–N(8)	177(1)

at 40 °C. These were continuously infused with a syringe pump (Harvard Apparatus, Model 22, South Natick, MA) at a typical flow rate of 2 μL min^{-1} into the pneumatically assisted electrospray probe with air as the nebulising gas. The optimum probe position was established from time to time, but was typically with the tip about 2 cm from the interface plate and with the spray off-axis from the orifice. Mass spectra were acquired in the positive-ion detection mode with unit resolution at a step size of 0.1 Th and at a dwell time of 10 ms per step. Typically, 10 scans were summed to produce a mass spectrum. Tandem mass spectrometry was performed with a nitrogen pressure of 2.5 mTorr in q2 and at a collision energy in the centre-of-mass frame (E_{cm}) of typically 4 eV.

Crystallography

All pertinent crystallographic data and other experimental details are summarised in Table 1. Measurements were made on a MAR research image plate scanner with graphite monochromated Mo-Kα radiation ($\lambda = 0.71069$ Å). The data were collected at a temperature of 25 ± 1 °C using the ω-scan technique (MAR). The data was corrected for Lorentz and polarisation effects. Absorption correction by the ψ-scan method or an approximation by inter-image scaling was applied. The structure was solved by Patterson methods (PATTY) and expanded using Fourier techniques.[9] The non-hydrogen atoms were refined anisotropically. Hydrogen atoms were included but not refined. All calculations were performed on a Silicon Graphics computer, using the program package TEXSAN.[10] The residual electron density peaks are relatively large; these are close to the heavy metal atoms.

CCDC reference number 440/208. See http://www.rsc.org/suppdata/nj/b0/b003673k/ for crystallographic files in .cif format.

Results and discussion

The compound [Ni(tren)Au(CN)$_2$][Au(CN)$_2$] (**1**) was obtained as light-purple crystals by reacting nickel(II) acetate with one equivalent of tren and one equivalent of K[Au(CN)$_2$] in aqueous solution. The structure was determined by X-ray crystallography; selected bond distances and angles are listed in Table 2. It consists of *cis*-[Ni(tren)]$^{2+}$ units linked by Au(CN)$_2^-$ to form infinite zig-zag chains (Fig. 1). Each Ni(tren)$^{2+}$ unit is also connected to an uncoordinated Au(CN)$_2^-$ through intermolecular N–H···N≡C hydrogen bonds. The Au(1)–Au(2) and Au(1*)–Au(3) distances are 3.5963(8) and 3.5932(8) Å, respectively, implying that Au···Au interactions are negligible. Each nickel(II) centre is coordinated to the four nitrogen atoms of the tren ligand and two nitrogen atoms cyanide groups. The Ni–N distances range from 2.09(1) to 2.14(1) Å for the Ni–N(tren), which are in the expected range for Ni–N(amine) bonds. The two Ni–N(CN) bonds and Ni–N–C(Au) bond angles are different. The Ni–N(5) bond length is 2.12(1) Å and the Ni–N(5)–C bond angle is 175(1)°, whereas the Ni–N(6) bond length [2.05(2) Å] is slightly shorter and the corresponding Ni–N(6)–C bond angle [169(1)°] deviates more from linearity. Both the bridging and the uncoordinated Au(CN)$_2^-$ are linear with similar Au–C and C–N bond lengths.

One-dimensional polymers are usually formed between bridging ligands and four-coordinate metal building blocks in

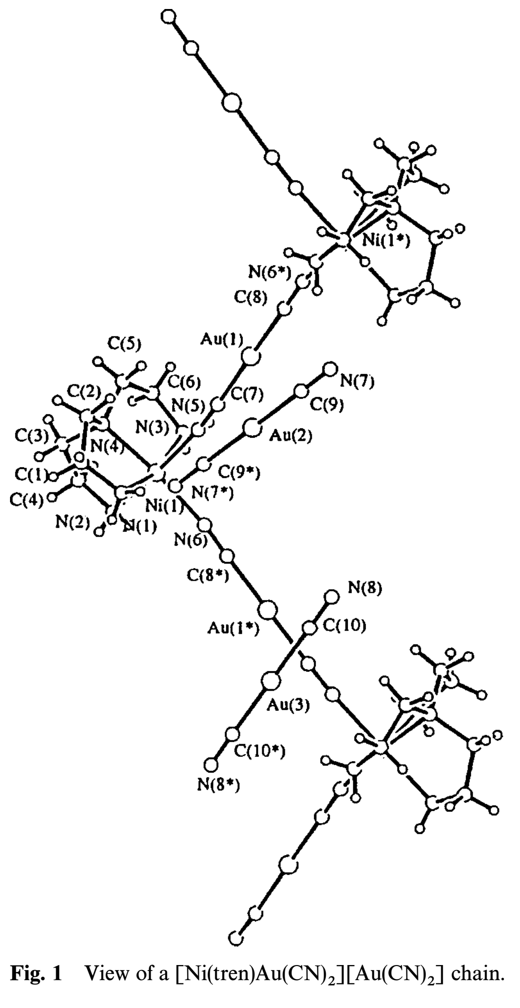

Fig. 1 View of a [Ni(tren)Au(CN)$_2$][Au(CN)$_2$] chain.

the *trans* configuration. In the present case, the use of the long and linear $Au(CN)_2^-$ ion enables a one-dimensional polymer to be formed from a bulky *cis*-metal building block. As far as we are aware, this is the first example of a polymer formed from a M(tren) building block; apart from monomeric complexes, only two dimeric structures, $[Cu_2(tren)_2(CN)_2]^{2+}$ and $[(tren)Cu(NC)Fe(CN)_4(CN)Cu(tren)] \cdot 12H_2O$, have been reported previously. The dimer $[Cu_2(tren)_2(CN)_2]^{2+}$ consists of two $[Cu(tren)(CN)]^+$ joined together by Cu–CN···HN–Cu hydrogen bonding.[11] Addition of $[Fe(CN)_6]^{4-}$ to $Cu(tren)^{2+}$ produced the complex $[(tren)Cu(NC)Fe(CN)_4(CN)Cu(tren)] \cdot 12\ H_2O$[12] rather than a polymeric species.

The IR spectrum (KBr) of **1** shows peaks at 2144 and 2179 cm^{-1}, which are assigned to $\nu(C{\equiv}N)$ of the bridging and the uncoordinated $[Au(CN)_2]^-$, respectively. The $\nu(C{\equiv}N)$ of $K[Au(CN)_2]^-$ is found at 2138 cm^{-1}. The $\nu(N–H)$ of **1** occurs at 3141 and 3272 cm^{-1}.

The magnetic susceptibility of the complex was studied in the temperature range 4–300 K (Fig. 2). The complex obeys the Curie–Weiss law throughout the temperature range, with a Curie constant of 1.10 cm^3 K mol^{-1} and a Weiss temperature, θ, of 0.62 K. The observed effective magnetic moment (μ_{eff}) of 2.97 μ_B at 299 K is slightly higher than the spin-only value of 2.83 and is within the expected range for high-spin Ni(II) complexes.

Although **1** was rather insoluble in all common solvents, an approximately 1 mmol dm^{-3} solution in water–methanol (1 : 1) could be obtained by warming the solution to *ca.* 40 °C. The dissolution of **1** was undoubtedly accompanied by a certain degree of depolymerisation, and the resulting species present in solution were studied by ESI-MS, which is now a well-established technique for extracting labile metal ions from solution with minimal fragmentation.[13–17] The electrospray mass spectrum of **1** in methanol–water (Fig. 3) shows peaks that can be represented by the general formulae $\{[Ni(tren)]_n[Au(CN)_2]_{2n-1}\}^+$ ($n = 1$–4) and $\{[Ni(tren)]_n[Au(CN)_2]_{2n-2}\}^{2+}$ ($n = 2$–9). Each 1+ peak is separated from the next one by 702 Th, corresponding to the difference in mass of one $\{Ni(tren)[Au(CN)_2]\}$ repeating unit. Similarly each 2+ peak is separated from the next by 351 Th.

The agreement between the experimental and calculated isotopic distribution patterns of all the ions is excellent. The ions $\{[Ni(tren)]_n[Au(CN)_2]_{2n-1}\}^+$ and $\{[Ni(tren)]_m[Au(CN)_2]_{2m-2}\}^{2+}$ ($m = 2n$) have the same nominal *m/z* values; they are, however, readily differentiated by their isotopic distribution patterns. Fig. 4 shows the isotopic distribution of the 1859.0 peak, together with theoretical distributions of pure $\{Ni_3(tren)_3[Au(CN)_2]_5\}^+$ and $\{Ni_6(tren)_6[Au(CN)_2]_{10}\}^{2+}$. After deconvolution, the experimental spectrum is found to be composed of approximately 55% $\{Ni_3(tren)_3[Au(CN)_2]_5\}^+$ and 45% $\{Ni_6(tren)_6[Au(CN)_2]_{10}\}^{2+}$. This is to be contrasted with the 455.3 and 1153.3 peaks, which are found to consist primarily of the 1+ ions, $[Ni(tren)Au(CN)_2]^+$ and $[Ni(tren)]_2[Au(CN)_2]_3{}^+$, respectively.

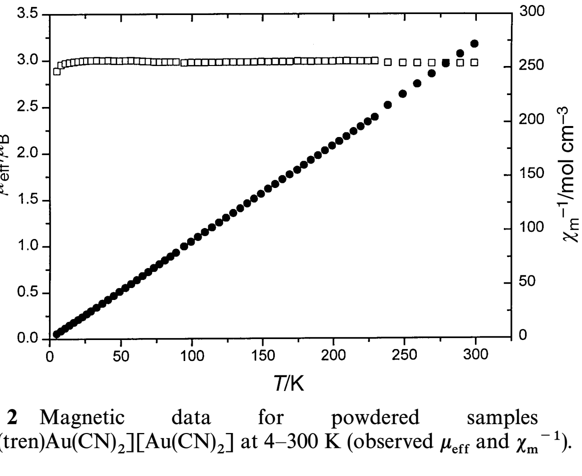

Fig. 2 Magnetic data for powdered samples of $[Ni(tren)Au(CN)_2][Au(CN)_2]$ at 4–300 K (observed μ_{eff} and $\chi_m{}^{-1}$).

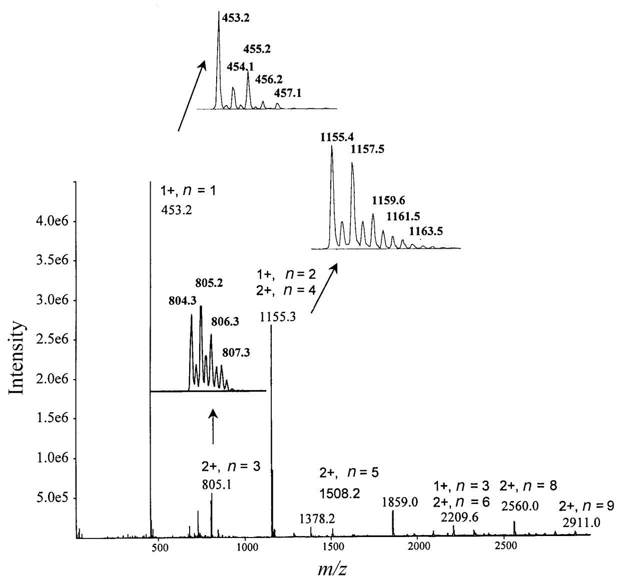

Fig. 3 Electrospray mass spectrum of $[Ni(tren)Au(CN)_2][Au(CN)_2]$ in 1 : 1 $H_2O–CH_3OH$. The peaks can be represented by the general formulae $\{[Ni(tren)]_n[Au(CN)_2]_{2n-1}\}^+$ (1+) and $\{[Ni(tren)]_n[Au(CN)_2]_{2n-2}\}^{2+}$ (2+). Insets show isotopic distributions of the major peaks.

Based on the crystal structure of the polymer, the ions in the electrospray ionisation mass spectrum of **1** are best described as composed of an oligomeric cation that may be associated with one or more $Au(CN)_2^-$ counter ions, such as

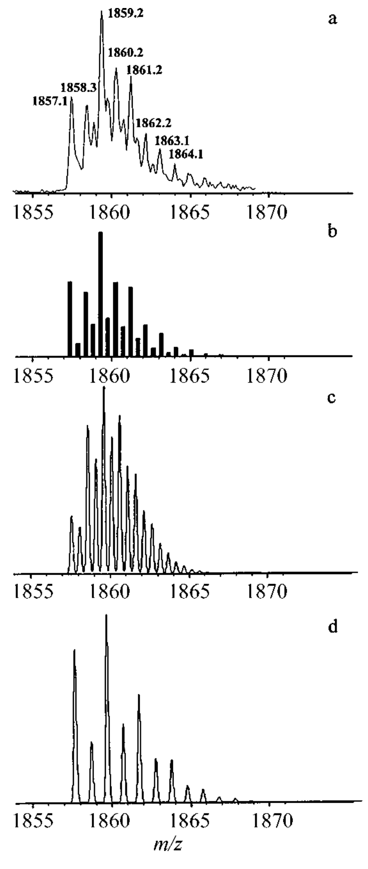

Fig. 4 (a) Expanded isotopic distribution of the cluster at 1859.0 Th; (b) sum of 55% (c) and 45% (d); (c) simulated isotopic distribution of $[Ni(tren)]_6[Au(CN)_2]_{10}{}^{2+}$; and (d) simulated isotropic distribution of $[Ni(tren)]_3[Au(CN)_2]_5{}^+$.

Table 3 Fragment ions of selected oligomeric ions

Precursor ion (*m*/*z*)	Fragment ions (*m*/*z*)	Assignment
$[\mathrm{Ni(tren)Au(CN)_2}]^+$ (453.2)	426.2	$[\mathrm{Ni(tren - H)Au(CN)}]^+$
	230.2	$[\mathrm{Ni(tren)CN}]^+$
	203.1	$[\mathrm{Ni(tren - H)}]^+$
	186.2	$[\mathrm{Ni(tren - H)}]^+ - \mathrm{NH_3}$
	160.2	$[\mathrm{Ni(tren - H)}]^+ - \mathrm{C_2H_5N}$
$\{[\mathrm{Ni(tren)}]_3[\mathrm{Au(CN)_2}]_4\}^{2+}$ (804.2)	1378.6	$\{[\mathrm{Ni(tren)}]_2\mathrm{Au_4(CN)_7}\}^+$
	1351.6	$\{[\mathrm{Ni(tren)}]_2\mathrm{Au_4(CN)_7}\}^+ - \mathrm{HCN}$
	1155.2	$\{[\mathrm{Ni(tren)}]_2[\mathrm{Au(CN)_2}]_3\}^+$
	1128.6	$\{[\mathrm{Ni(tren)}]_2[\mathrm{Au(CN)_2}]_3\}^+ - \mathrm{HCN}$
	1101.2	$\{[\mathrm{Ni(tren)}]_2[\mathrm{Au(CN)_2}]_3\}^+ - 2\ (\mathrm{HCN})$
	453.0	$[\mathrm{Ni(tren)Au(CN)_2}]^+$
	230.0	$[\mathrm{Ni(tren)CN}]^+$
	203.0	$[\mathrm{Ni(tren - H)}]^+$
$\{[\mathrm{Ni(tren)}]_2[\mathrm{Au(CN)_2}]_3\}^+$ (1155.4)	1128.2	$\{[\mathrm{Ni(tren)}]_2[\mathrm{Au(CN)_2}]_3\}^+ - \mathrm{HCN}$
	1101.2	$\{[\mathrm{Ni(tren)}]_2[\mathrm{Au(CN)_2}]_3\}^+ - 2\ \mathrm{HCN}$
	1074.2	$\{[\mathrm{Ni(tren)}]_2[\mathrm{Au(CN)_2}]_3\}^+ - 3\ \mathrm{HCN}$
	903.4	$\{[\mathrm{Ni_2(tren)(tren - H)}][\mathrm{Au(CN)_2}]_2\}^+ - \mathrm{H_2}$
	876.3	903.4 − HCN
	849.2	903.4 − 2 HCN
	453.2	$[\mathrm{Ni(tren)Au(CN)_2}]^+$
	426.2	$[\mathrm{Ni(tren - H)Au(CN)}]^+$
	230.2	$[\mathrm{Ni(tren)CN}]^+$
	203.1	$[\mathrm{Ni(tren - H)}]^+$
	186.2	$[\mathrm{Ni(tren - H)}]^+ - \mathrm{NH_3}$
	160.3	$[\mathrm{Ni(tren - H)}]^+ - \mathrm{C_2H_5N}$

$\{[\mathrm{Ni(tren)}]_n[\mathrm{Au(CN)_2}]_{n+1}\}\cdot x[\mathrm{Au(CN)_2}]^-$, where $x = n - 2$ for the 1+ ions and $x = n - 3$ for the 2+ ions. The 1+ ion with $n = 1$ is simply the binuclear species $[\mathrm{Ni(tren)N{\equiv}C{-}Au{-}C{\equiv}N}]^+$. This hypothesis is supported by the results of tandem mass spectrometry. Table 3 shows the most abundant fragment ions of $[\mathrm{Ni(tren)Au(CN)_2}]^+$, $\{[\mathrm{Ni(tren)}]_3[\mathrm{Au(CN)_2}]_4\}^{2+}$ and $\{[\mathrm{Ni(tren)}]_2[\mathrm{Au(CN)_2}]_3\}^+$; the product ion spectrum of $\{[\mathrm{Ni(tren)}]_3[\mathrm{Au(CN)_2}]_4\}^{2+}$ is shown in Fig. 5 as an example. Fragmentation of $\{[\mathrm{Ni(tren)}]_3[\mathrm{Au(CN)_2}]_4\}^{2+}$ yields abundant product ions. The ions at 230 and 1378.6 Th, assigned as $[\mathrm{Ni(tren)CN}]^+$ and $\{[\mathrm{Ni(tren)}]_2\mathrm{Au_4(CN)_7}\}^+$, may be regarded as a pair of products formed simultaneously from the fragmentation of $\{[\mathrm{Ni(tren)}]_3[\mathrm{Au(CN)_2}]_4\}^{2+}$ [(230.0 + 1378.6)/2 = 804.3 Th]. Similarly, the ions at 453 and 1155 Th, $[\mathrm{Ni(tren)Au(CN)_2}]^+$ and $\{[\mathrm{Ni(tren)}]_2[\mathrm{Au(CN)_2}]_3\}^+$, may also be regarded as being formed simultaneously from $\{[\mathrm{Ni(tren)}]_3[\mathrm{Au(CN)_2}]_4\}^{2+}$ [(453.0 + 1155.2)/2 = 804.1 Th]. Furthermore, there are minor product ions that appear to form by elimination of $\mathrm{HAu(CN)_2}$ and HCN from some of the product ions, for example the $[\mathrm{Ni(tren - H)}]^+$ ion at 203 Th may be formed from the $[\mathrm{Ni(tren)Au(CN)_2}]^+$ ion at 453 Th after elimination of $\mathrm{HAu(CN)_2}$. This observation is another example of our earlier findings in which an amino hydrogen in the ligand tren (and in 1,4,8,11-tetraazacyclotetradecane, cyclam, as well) in a collisionally activated Ni- and Cu-containing macrocyclic complex ion is capable of being abstracted by an anion adducted to the complex.[18]

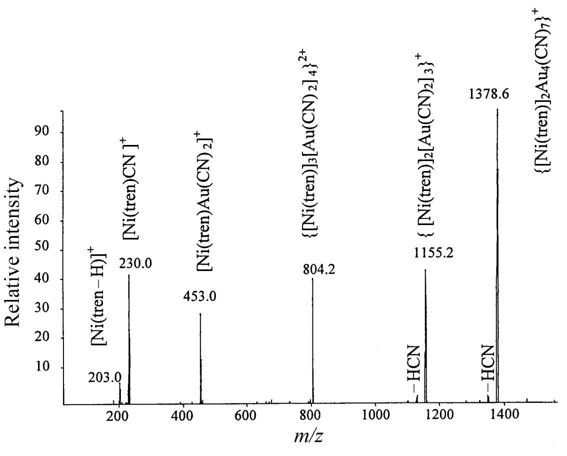

Fig. 5 Product ion spectrum of $\{[\mathrm{Ni(tren)}]_3[\mathrm{Au(CN)_2}]_4\}^{2+}$.

In conclusion, the long and linear structure of $\mathrm{Au(CN)_2}^-$ makes it useful as a bridging ligand for the construction of novel polymeric materials, especially from bulky metal building blocks. Ionic oligomeric metal complexes can be readily characterised in solution using ESI-MS as well as tandem mass spectrometry. This should provide useful information on the structure of the polymer, especially in cases where the crystal structure is not available.

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