A telluride capped trinuclear nickel cluster $[Ni_3(\mu_3\text{-}Te)_2(\mu\text{-}PPh_2CH_2PPh_2)_3]^{n+}$ with four accessible redox states ($n = -1, 0, 1, 2$)

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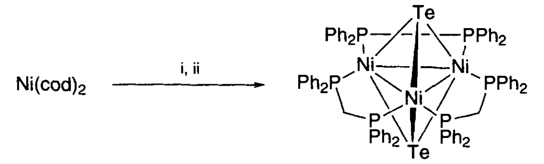
The new telluride capped trinuclear nickel cluster $[Ni_3(\mu_3\text{-}Te)_2(\mu\text{-dppm})_3]$ 1 is prepared from $TePPr^n_3$, bis(cycloocta-1,5-diene)nickel(0), and dppm [bis(diphenylphosphino)methane]; results of cyclic voltammetry studies establish that 1 has a capacity for multiple electron transfer through three reversible redox couples spanning the states 1^-, 1, 1^+, and 1^{2+}; cluster 1^+ is characterized by X-ray crystallography.

Metal cluster compounds potentially can undergo the multiple electron transfers required in such important chemical transformations as water oxidation (4 e^-),[1,2] nitrogen reduction to ammonia (6 e^-),[3–8] or CO_2 reduction to methane (8 e^-).[9–11] The chemistry of trinuclear nickel clusters supported by dppm has been an area of interest in our laboratory.[12–20] The clusters $[Ni_3(\mu_3\text{-}CNR)(\mu_3\text{-}I)(\mu\text{-dppm})_3]PF_6$ are electrocatalysts for the reduction of CO_2 to CO and CO_3^{2-} (a 2 e^- process), but they are inefficient catalysts because they function through a single electron redox cycle, $E_{1/2}$ $[\{Ni_3(\mu_3\text{-}CNR)(\mu_3\text{-}I)(\mu\text{-dppm})_3\}^{+/0}]$.[16,17] We report here the synthesis, electrochemistry, and structure of $[Ni_3(\mu_3Te)_2(\mu\text{- dppm})_3]$ **1**, a chalcogenide capped, diphosphine bridged nickel cluster. In particular, we find that cluster **1** has a greater capacity for multiple electron transfer compared to either the μ_3-CNR, μ_3-I or the $(\mu_3\text{-}I)_2$ trinuclear nickel clusters reported previously.[12–20]

Reaction of 1 equiv. of $Ni(cod)_2$ with 1 equiv. of dppm in toluene gives a red–orange solution attributed to the formation of $Ni_2(dppm)_3$.[21] Addition of 2–3 equiv. of the 'Te atom transfer reagent', $TePPr^n_3$,[22,23] in toluene results in a black solution (Scheme 1). Reducing the solvent volume under vacuum leads to precipitation of a black solid. A FABMS study of this material yields a spectrum with *m/z* 1583.2 and a unit resolution isotopic distribution pattern consistent with the formula $C_{75}H_{66}Ni_3P_6Te_2$. The cyclic voltammogram of **1** in MeCN (Fig. 1) exhibits three reversible electrochemical couples $E_{1/2}$ ($1^{2+/+}$) = +0.28; $E_{1/2}$ ($1^{2+/+}$) = −0.52 and $E_{1/2}$ ($1^{0/+}$) = −1.31 V *vs.* SCE (Scheme 2). The magnetic susceptibility, as determined by the Evans method,[24,25] is consistent with an S = 1 system. This is consonant with recently reported results of extended Hückel molecular orbital calculations for the related 52 e^- cluster, $[Ni_3(\mu_3\text{-}I)_2(\mu\text{-dppm})_3]$, which indicate an e^4 ground state.[12] Thus, the 50 e^- cluster **1** is expected to have an e^2 ground state electronic configuration with two unpaired electrons. Cluster **1** was oxidized with either 1 or 2 equiv. of $[Fe(\eta\text{-}C_5H_5)_2]PF_6$ to yield $[Ni_3(\mu_3\text{-}Te)_2(\mu\text{-dppm})_3]^+$ (1^+) or $[Ni_3(\mu_3\text{-}Te)_2(\mu\text{-dppm})_3]^{2+}$ (1^{2+}), respectively. The magnetic susceptibility measurement (Evans method) of 1^+ indicated an S = 1/2 system. A singlet at δ 60.1 was observed in the ^{31}P NMR spectrum of 1^{2+}, consistent with its formulation as a diamagnetic 48 e^- cluster. Attempts to alkylate or protonate the capping tellurides of **1** with $MeSO_2C_6H_4Me$, Me_3OBF_4, HCl, or $PhCH_2Cl$ led only to the oxidation of the cluster to produce 1^+. Similarly, reaction of 1^{2+} with PhLi led to the formation of 1^+. We note that the related clusters, $[Ni_3(\mu_3\text{-}S)_2(\eta^2\text{-dppe})_3]^{2+}$ and $[Ni_3(\mu_3\text{-}Se)_2(\eta^2\text{-dppe})_3]^{2+}$, exhibit two reversible reductions in their electrochemistry [dppe = 1,2-bis(diphenylphosphino)ethane].[26] These results underscore the predominance of electron transfer in the chemistry of these clusters.



Scheme 1 *Reagents and conditions*: i, dppm, toluene; ii, $Te{=}PPr^n_3$, toluene

X-Ray quality crystals of $[Ni_3(\mu_3\text{-}Te)_2(\mu_2\text{-dppm})_3]Cl$ **1Cl** were grown from CH_2Cl_2–pentane. Results of the X-ray diffraction study confirm that 1^+ is a chalcogenide capped nickel trimer containing bridging phosphine ligands.‡ This contrasts to the structurally characterized chalcogenide capped nickel trimers $[Ni_3(\mu_3\text{-}Se)_2(PEt_3)_6]^{2+}$, $[Ni_3(\mu_3\text{-}Se)_2(PEt_3)_6]^{2+}$, $[Ni_3(\mu_3\text{-}S)_2(\eta^2\text{-dppe})_3]^{2+}$, and $[Ni_3(\mu_3\text{-}Se)_2(\eta^2\text{-dppe})_3]^{2+}$ which contain either monodentate phosphine ligands or chelating diphosphine ligands.[26–28] An ORTEP drawing of the molecular cation, 1^+, is presented in Fig. 2. Average Ni–Ni distances of 2.56(3) Å are found for 1^+. This is similar to the average Ni–Ni distances of 2.49(2) and 2.52(1) Å for $[Ni_3(\mu_3\text{-}I)_2(\mu\text{-dppm})_3]$ and $[Ni_3(\mu_3\text{-}I)_2(\mu\text{- dppm})_3]^+$, respectively,[12] but significantly shorter than the average Ni–Ni distances of 2.91(4), 3.16(5), 2.83(2) and 3.00(9) Å for $[Ni_3(\mu_3\text{-}S)_2(PEt_3)_6]^{2+}$, $[Ni_3(\mu_3\text{-}Se)_2(PEt_3)_6]^{2+}$, $[Ni_3(\mu_3\text{-}S)_2(\mu^2\text{-dppe})_3]^{2+}$ and $[Ni_3(\mu_3\text{-}Se)_2(\eta^2\text{-dppe})_3]^{2+}$ respectively.[26–28] The geometries of each of these structures have been described as three NiP_2 units sharing two capping atoms.[26–28] It appears that the presence of bridging dppm ligands in $[Ni_3(\mu_3\text{- }I)_2(\mu\text{-dppm})_3]$, $[Ni_3(\mu_3\text{-}I)_2(\mu\text{-dppm})_3]^+$, and 1^+ is the single most important factor for determining whether short or long nickel–nickel distances will occur in $(\mu_3\text{-}X)_2$ or $(\mu_3\text{-}E)_2$ capped trinuclear nickel clusters. The average Ni–Te distance, 2.50(1) Å, for 1^+ is shorter than the average Ni–I distance, 2.65(4) Å, for $[Ni_3(\mu_3\text{-}I)_2(\mu\text{-dppm})_3]^+$

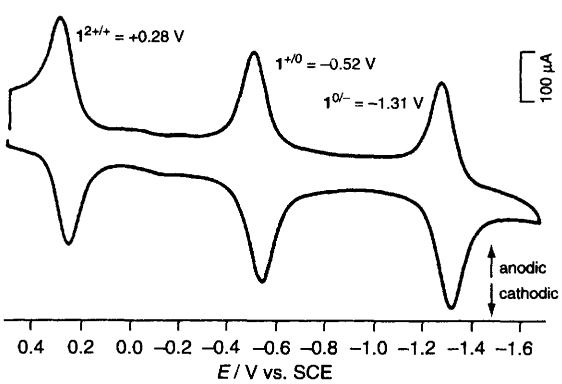


Fig. 1 Cyclic voltammogram of $[Ni_3(\mu_3\text{-}Te)_2(\mu\text{-dppm})_3]$ in 0.1 mol dm^{-3} NBu_4PF_6–MeCN. The scan rate was 100 mV s^{-1} and the potential is referenced to the saturated calomel electrode (SCE).

$$1^{2+} \underset{}{\overset{+0.28}{\rightleftharpoons}} 1^{+} \overset{-0.52}{\rightleftharpoons} 1 \overset{-1.31}{\rightleftharpoons} 1^{-}$$

Scheme 2 *E*/V *vs.* SCE

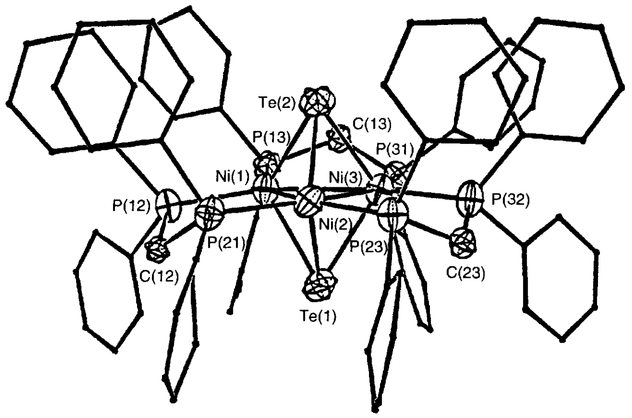


Fig. 2 ORTEP drawing of $[Ni_3(\mu_3\text{-}Te)_2(\mu\text{-}dppm)_3]Cl{\cdot}3CH_2Cl_2$. Bond distances (Å): Ni(1)–Ni(2) 2.568(7), Ni(1)–Ni(3) 2.533(6), Ni(2)–Ni(3) 2.595(6), Te(1)–Ni(1) 2.506(4), Te(1)–Ni(2) 2.520(5), Te(1)–Ni(3) 2.495(5), Te(2)–Ni(1) 2.477(5), Te(2)–Ni(2) 2.489(5), Te(2)–Ni(3) 2.496(5), mean Ni–P 2.23(1).

which in turn is slightly shorter than the average Ni–I distance, 2.71(3) Å, for $[Ni_3(\mu_3\text{-}I)_2(\mu\text{-}dppm)_3]$. This is expected as $[Ni_3(\mu_3\text{-}I)_2(\mu\text{-}dppm)_3]^+$ and $[Ni_3(\mu_3\text{-}I)_2(\mu\text{-}dppm)_3]$ have 51 and 52 electron cores respectively,[12] while $[Ni_3(\mu_3\text{-}Te)_2(\mu\text{-}dppm)_3]^+$ contains a 49 electron core. The HOMOs of both $[Ni_3(\mu_3\text{-}Te)_2(\mu\text{-}dppm)_3]$ and $[Ni_3(\mu_3\text{-}I)_2(\mu\text{-}dppm)_3]$[12] show substantial nickel-capping ligand antibonding interactions. Removal of electrons from the e^4 ground state of $[Ni_3(\mu_3\text{-}I)_2(\mu\text{-}dppm)_3]$ to give the e^3 ground state of $[Ni_3(\mu_3\text{-}I)_2(\mu\text{-}dppm)_3]^+$, then the e^2 ground state of $[Ni_3(\mu_3\text{-}Te)_2(\mu\text{-}dppm)_3]$, and finally the e^1 ground state of $[Ni_3(\mu_3\text{-}Te)_2(\mu\text{-}dppm)_3]^+$ results in successively less metal–capping ligand antibonding interactions. Hence, the removal of electrons from the core results in a shortening of the nickel to capping ligand distances.

$[Ni_3(\mu_3\text{-}Te)_2(\mu\text{-}dppm)_3]$ **1** is a highly redox active metal cluster exhibiting reversible electrochemistry and chemistry dominated by electron transfer. Cluster **1** in its various redox states $\mathbf{1}^-$, **1**, $\mathbf{1}^+$, and $\mathbf{1}^{2+}$ is part of a larger family of nickel trimers of the general formula $[Ni_3(\mu_3\text{-}L)_2(\mu\text{-}dppm)_3]^{n+}$. The series extends from the Ni_3^{6+} core of the 48 electron cluster $\mathbf{1}^{2+}$, includes the Ni_3^{5+} core of $\mathbf{1}^+$, Ni_3^{4+} core of **1**, intersects in the cases of the cores of the Ni_3^3 51 electron clusters $\mathbf{1}^-$ and $[Ni_3(\mu_3\text{-}I)_2(\mu\text{-}dppm)_3]^+$,[12] and continues to the Ni_3^{2+} and Ni_3^+ clusters $[Ni_3(\mu_3\text{-}I)_2(\mu\text{-}dppm)_3]$ and $[Ni_3(\mu_3\text{-}CNR)(\mu_3\text{-}I)(\mu\text{-}dppm)_3]$,[12,14] respectively.

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Footnotes

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‡ *Crystal data* for $[Ni_3(\mu_3\text{-}Te)_2(\mu\text{-}Te)_2(\mu\text{-}dppm)_3]Cl{\cdot}3CH_2Cl_2$: $C_{78}H_{72}Cl_7Ni_3Te_2$, monoclinic, space group Pn, a = 11.083(2), b = 15.491(3), c = 22.874(3) Å, β = 90.89(1)°, M = 1874.79, U = 3926(2) $Å^3$, $Z = 2$, D_c = 1.585 g cm^{-3}, T = 295 K, $F(000)$ = 1874.0, R = 0.054 [2402 reflections with $I > 3.0\sigma(I)$], R_w = 0.059 for 5513 unique reflections with 473 variables. A needle measuring 0.25 × 0.10 × 0.10 mm was mounted on a glass fibre and diffraction data were collected on an Enraf-Nonius CAD4 computer equipped with graphite-monochromated Cu-Kα radiation (λ = 1.5484 Å). Solution of structure was by direct methods (SHELX-86),[29] and refinement was by full-matrix least squares as per Killean and Lawrence.[30] Refinement was done using MolEN.[31] Atomic coordinates, bond lengths, and angles, and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre (CCDC). See Information for Authors, Issue No. 1. Any request to the CCDC for this material should quote the full literature citation and the reference number 182/112.

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