[{(tBuC$_5$H$_4$)$_2$Nb(CO)}$_3$Co$_9$(CO)$_8$Te$_6$ · 3Cr(CO)$_5$]: Unusual Stabilization of a Cubic Body-Centered Metal Telluride Cluster by Peripheral Complex Fragments**

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Transition metal clusters, which contain M$_8$ cubes with heavy main group elements as bridging ligands, serve as simple models for solid-state structures.[1] Clusters of the type [M$_9$L$_8$(μ_4-E)$_6$] (M = Ni, Pd; L = PPh$_3$, CO, Cl; E = GeEt,[2] As,[3] Sb,[4] Te[5]) are characterized by an additional metal atom in the center of the cluster. The first cobalt-containing representative of the [M$_9$L$_8$(μ_4-E)$_6$] class of compounds is the cluster salt [(C$_5$Me$_5$)$_2$Nb(CO)$_2$]$_2$[Co$_9$(CO)$_8$Te$_6$] ([(C$_5$Me$_5$)$_2$Nb(CO)$_2$]$_2$ (**1**)), which was only obtained in very low yields, so that it is impossible to further investigate its chemical properties.[6] We now report on a rational synthesis of a cluster, that is closely related to the anion [**1**]$^{2-}$, but whose metal telluride sphere is expanded by peripheral transition metal complex fragments.

The reaction of [Cp$'_2$Nb(Te$_2$)H] (Cp$'$ = tBuC$_5$H$_4$)[7] with two equivalents of [Co$_2$(CO)$_8$] in boiling toluene gave the dark red neutral compound [{Cp$'_2$Nb(CO)}$_3$Co$_9$(CO)$_8$Te$_6$] (**2**) in good yield after chromatographic work-up on silica gel. As mass spectra of **2** could not be obtained, its composition was derived from an X-ray diffraction analysis of the Cr(CO)$_5$-adduct **3** (see below) and confirmed by C, H analyses. The IR spectrum of **2** exhibits three bands at 2005, 1965, and 1915 cm^{-1} typical of terminal CO absorptions, along with the characteristic ν(C–H) frequencies of the tBuC$_5$H$_4$ groups. The CO pattern may be explained by the presence of nonequivalent sets of Co(CO) and Cp$'_2$Nb(CO) units.[8]

Complex **2** reacted with an excess of [Cr(CO)$_5$(thf)] in THF solution to give the red-brown complex **3** and dark brown **4**. Both compounds were purified by column chromatography without decomposition. The composition of **3** was determined by means of X-ray crystallography and the resulting formula [{Cp$'_2$Nb(CO)}$_3$Co$_9$(CO)$_8$Te$_6$ · 3Cr(CO)$_5$] was confirmed by C, H analyses. The dark brown compound **4** could not yet be structurally characterized, but according to its IR spectrum it contains Cr(CO)$_5$ groups, and C,H analyses are in agreement with the formula [{Cp$'_2$Nb(CO)}Co$_9$(CO)$_8$Te$_6$ · 3Cr(CO)$_5$]. The IR spectrum of **3** exhibits a pattern in the region of the terminal CO absorptions which may be interpreted as the sum of the bands of **2** and those of the coordinated Cr(CO)$_5$ fragments (2055 cm^{-1}). Complex **4** reveals a very similar pattern.

Inspite of intense efforts single crystals of **3** were obtained only as very thin needles, and the crystallographic study[9] suffered accordingly from the low quality of the crystals. Whereas the heavy atoms could be refined anisotropically, the identification of the solvent molecules in the crystal was problematic. The dominating structural feature of the molecule is a Co$_8$ cube, which contains a central cobalt atom (Figure 1). The faces of the cube are bridged by six Te ligands,

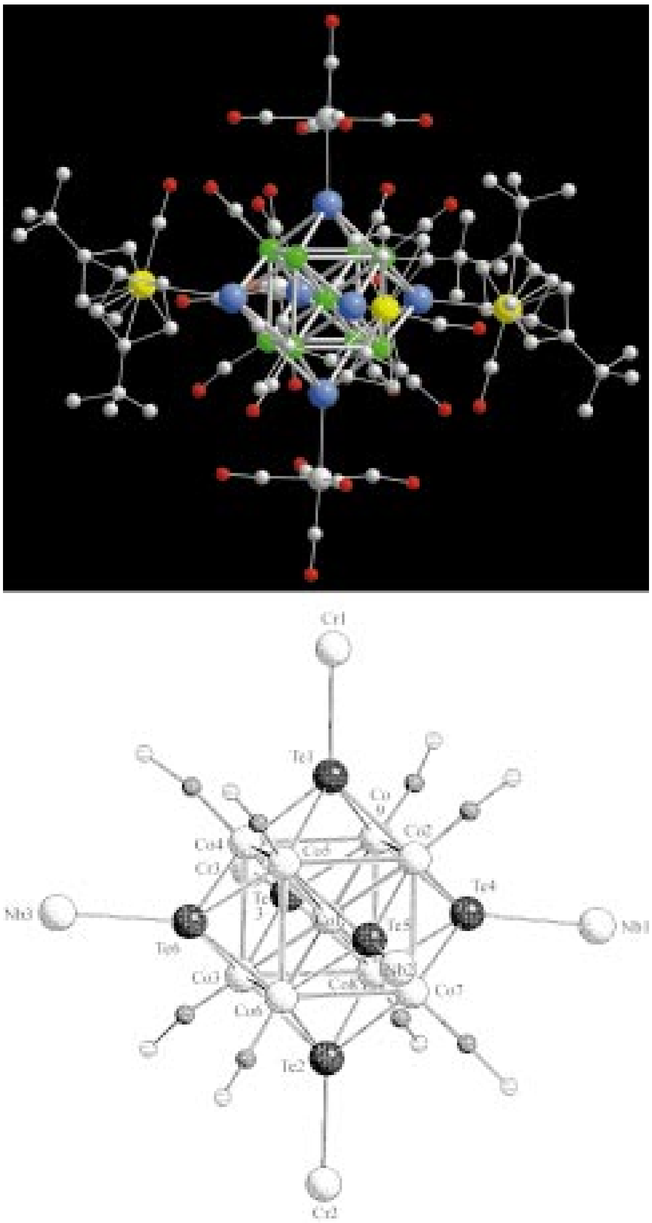

Figure 1. Structure of **3** in the crystal. Top: overview; bottom: [Co$_9$(CO)$_8$Te$_7$] core with attached Cr and Nb atoms, which denote Cr(CO)$_5$ and Cp$'_2$Nb(CO) fragments, respectively. Selected distances [Å] and angles [°]: Co1-Te1 2.925(4), Co1-Te2 2.912(4), Co1-Te3 2.927(3), Co1-Te4 2.956(5), Co1-Te5 2.928(3), Co1-Te6 2.940(5), Co1-Co2 2.395(5), Co1-Co3 2.408(5), Co1-Co4 2.382(6), Co1-Co5 2.394(5), Co1-Co6 2.386(4), Co1-Co7 2.381(6), Co1-Co8 2.412(5), Co2-Te1 2.488(5), Co2-Co5 2.778(9), Co2-Co9 2.741(8), Co3-Te2 2.505(5), Co4-Te1 2.479(4), Co4-Te3 2.477(4), Co4-Co5 2.754(4), Co5-Te1 2.492(3), Co6-Te2 2.475(4), Co7-Te2 2.474(3), Co8-Te2 2.489(3), Co8-Te4 2.481(4), Co9-Te1 2.490(4), Cr1-Te1 2.643(6), Cr2-Te2 2.638(5), Cr3-Te3 2.633(4), Nb1-Te4 2.860(4), Nb2-Te5 2.871(3), Nb3-Te6 2.837(4); Co3-Co1-Co5 109.5(2), Co4-Co1-Co7 179.7(2), Co5-Co1-Co6 71.0(2), Te1-Co1-Te2 179.6(2), Te1-Co1-Te4 90.3(2), Te4-Co1-Co8 53.9(2), Te5-Co2-Co1 73.0(2), Te1-Co4-Te6 113.0(2), Co4-Te1-Co5 67.3(2), Co1-Te1-Cr1 128.5(2), Co1-Te2-Cr2 176.3(2), Co1-Te5-Nb2 174.6(2), Co1-Te6-Nb3 174.2(2).

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to which three $\mathrm{Cp'_2Nb(CO)}$ and three $\mathrm{Cr(CO)_5}$ fragments are coordinated. These groups are arranged in a meridional manner with respect to the $\mathrm{Te_6}$ octahedron. Inspite of the relatively low quality of the structure solution a comparison of bond parameters of **3** and $[\mathbf{1}]^{2-}$ reflects a weak, but unequivocal trend, which may be interpreted as a slight contraction of the $\mathrm{Co_9Te_6}$ cube in **3**: 1) The distances of each Te bridge from the corners of the $\mathrm{Co_8}$ cage in **3** are on average 0.03 Å shorter than in $[\mathbf{1}]^{2-}$, a similar trend is observed for the distances of the Te atoms from the central Co1 atom; 2) the Co–Co edges in **3** (mean 2.76(1) Å) are 0.01 Å shorter than in $[\mathbf{1}]^{2-}$, as are the distances of Co1 from the corners of the cube.

The Nb–Te distances (mean 2.856 Å) are typical of Nb–Te single bonds.[3, 10] The Cr–Te distances (mean 2.638(5) Å) are about 0.1 Å shorter than those in anionic chromium tellurides,[11] but slightly longer than those in [*cyclo*-$\mathrm{Te_4\{Cr(CO)_5\}_4}$].[12] The contribution of the $\mathrm{Cr(CO)_5}$ fragments in stabilizing the $\mathrm{Co_9Te_6}$ cube is still a matter of speculation, but there is no doubt that they improve considerably the crystallization properties of the resulting product **3**.

Each of the three niobocenecarbonyl units in **2** and **3** acts as a 17-electron fragment, which is anchored covalently to the cluster core through the Te ligands. Complex **4**, however, contains only one of these units. Consequently, each of the Te ligands linked to Nb centers contributes five electrons to the metal valence electrons (MVE) of the cluster. The other Te ligands provide only four electrons each, whereas their lone pair of electrons may stabilize "outer" unsaturated complex fragments as realized in **3**. This results in 124 MVE ($(9 \times 9$ for Co) + $(8 \times 2$ for CO) + $(3 \times 5$ for μ_5-Te) + $(3 \times 4$ for μ_4-Te)) for the $\mathrm{Co_9(CO)_8Te_6}$ core in **2** (and analogously in **3**). By comparison the cluster core of **4** contains 122 MVE and that of $[\mathbf{1}]^{2-}$ 123 MVE.

The observed weak contraction of the $\mathrm{Co_9Te_6}$ cube, when comparing the structural parameters of $[\mathbf{1}]^{2-}$ and **3**, is qualitatively supported by density functional theory (DFT) calculations. These have been carried out on the structure model of the $\mathrm{Co_9(CO)_8Te_6}$ cluster core bearing two- and threefold negative charge, for example $[\mathbf{1}]^{2-}$[6] and $[\mathbf{1}]^{3-}$. The MO scheme of $[\mathbf{1}]^{3-}$ is built up as following: Its HOMO, which is already known from $[\mathbf{1}]^{2-}$ to contain a high Co1-d_{z^2} orbital portion as well as significant s/p contributions of the axial Te atoms in a_{1g} symmetry, incorporates the additional valence electron of the $\mathrm{Co_9Te_6}$ core. The resulting higher electron density of the $a_{1g}(\mathrm{d}_{z^2})$ state along with the similar energetic level of the $\mathrm{d}_{x^2-y^2}$ and d_{z^2} orbitals in $[\mathbf{1}]^{3-}$ should slightly enhance the interaction between Co1 and the six Te atoms.

The reaction of $[\mathrm{Cp'_2Nb(Te_2)H}]$ with $[\mathrm{Co_2(CO)_8}]$ is strongly temperature dependent. At 0 °C $[\mathrm{Co_4(CO)_{10}Te_2}]$[13] and low quantities of $[\mathrm{\{Cp'_2Nb(CO)\}Co_3(CO)_6Te_2}]$ are formed. The latter contains, like its peralkylated analogue,[6] a trigonal-bipyramidal $\mathrm{Co_3(CO)_6Te_2}$ cluster to which a $\mathrm{Cp'_2Nb(CO)}$ fragment is connected through an apical Te ligand. At higher temperature the neutral cluster **2** is formed. This is in strong contrast to the system $[\mathrm{(C_5Me_5)_2Nb(Te_2H)}]/[\mathrm{Co_2(CO)_8}]$, which gives rise to the formation of salts that are built up from pentagonal-prismatic $[\mathrm{Co_{11}(CO)_{10}Te_7}]^{n-}$ ions ($n = 1, 2$)[6] and $[\mathrm{(C_5Me_5)_2Nb(CO)_2}]^+$ ions. The formation of such different cluster skeletons may be a consequence of the different structures of the employed niobocene tellurides.[7]

In contrast to the salt $[\mathrm{(C_5Me_5)_2Nb(CO)_2}]_2$-**1**, complexes **2** and **3** are of covalent nature. Cluster **2** may be considered as a potential precursor of the hypothetical compound $[\mathrm{Cp'_2Nb(CO)_2}]_3[\mathrm{Co_9(CO)_8Te_6}]$, containing $[\mathbf{1}]^{3-}$ as cluster anion. Attempts to prepare this salt, starting from **2** by high-pressure carbonylation (200 bar CO, THF) of the niobocene component, gave thus far only $[\mathrm{Co_4(CO)_{10}Te_2}]$.[13] Further experiments to synthesize the anion $[\mathbf{1}]^{3-}$ are planned, mainly to establish the presumed redox relationship with the above-mentioned $[\mathbf{1}]^{2-}$. However, the formation of the niobocene dicarbonyl cation $[\mathrm{Cp_2Nb(CO)_2}]^+$ ($\mathrm{Cp} = \mathrm{Cp'}$, $\mathrm{C_5Me_5}$), which is responsible for the charge separation in $[\mathrm{(C_5Me_5)_2Nb(CO)_2}]_2$ (**1**), may be favored in the case of the more electron-rich $\mathrm{C_5Me_5}$ ligand.

The reaction of $[\mathrm{Cp'_2Nb(Te_2)H}]$ with $[\mathrm{Co_2(CO)_8}]$ provides an efficient access to cubic metal-centered cobalt telluride clusters. Anchoring of peripheral complex fragments permits the realization of clusters with different charge and electron counts. Finally, the expeceted reactivity potential of **2** may extend the knowledge on the chemistry of metal telluride clusters.

Experimental Section

2: The mixture of $[\mathrm{Cp'_2Nb(Te_2)H}]$ (550 mg, 0.930 mmol),[7] $[\mathrm{Co_2(CO)_8}]$ (640 mg, 1.872 mmol), and toluene (100 mL) was stirred for 3 h at 110 °C. After the mixture had been cooled to room temperature, the solvent was removed and the residue dissolved in THF (15 mL). Chromatography on $\mathrm{SiO_2}$ (activity II-III, column 15 cm, ∅ 3 cm) with THF gave a broad dark red band that contained **2** (630 mg, 0.241 mmol; 78 %). Recrystallization of **2** from THF/pentane (5:1) gave fine dark needles. Elemental analysis (%) calcd for $\mathrm{C_{65}H_{78}Co_9Nb_3O_{11}Te_6}$ (2609.97): C 29.91, H 3.01; found: C 29.63, H 3.37; IR (KBr): $\tilde{\nu}(\mathrm{CO}) = 2005$ (m), 1965 (vs), 1915 (vs) $\mathrm{cm^{-1}}$.

$[\mathrm{\{Cp'_2Nb(CO\}_{\mathit{x}}Co_9(CO)_8Te_6 \cdot 3\,Cr(CO)_5}]$ ($x = 3$: **3**; $x = 1$: **4**): A solution of $[\mathrm{Cr(CO)_5(thf)}]$ (1.45 mmol) in THF (150 mL) was added to the dark red solution of **2** (630 mg, 0.241 mmol) in THF (30 mL) and stirred in the dark for 12 h at room temperature. After evaporation of the solvent the residue was dissolved in THF (12 mL) and chromatographed on $\mathrm{SiO_2}$ (column 20 cm, ∅ 5 cm). A red-brown band was eluted with THF which contained **3** (560 mg, 0.193 mmol; 68 %), whereas weakly colored bands eluted with THF/acetone (4:1) were not isolated. The dark brown complex **4** was eluted with THF/acetone (1:1) in 270 mg yield. Recrystallization of **3** from $\mathrm{CH_2Cl_2}$/toluene (1:1) gave dark red crystals. **3**: Elemental analysis (%) calcd for $\mathrm{C_{80}H_{78}Co_9Cr_3Nb_3O_{26}Te_6}$ (3186.12): C 30.16, H 2.47; found: C 30.66, H 2.66; IR (KBr): $\tilde{\nu}(\mathrm{CO}) = 2055$ (s), 2005 (m), 1960 (vs), 1920 (vs) $\mathrm{cm^{-1}}$. **4**: Elemental analysis (%) calcd for $\mathrm{C_{42}H_{26}Co_9Cr_3NbO_{24}Te_6}$ (2677.9): C 20.52, H 1.07; found: C 21.06, H 1.68; IR (KBr): $\tilde{\nu}(\mathrm{CO}) = 2050$ (s), 2010 (m), 1965 (vs), 1930 (vs) $\mathrm{cm^{-1}}$.

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[9] Crystal structure analysis of **3**: dark red crystals, $0.20 \times 0.08 \times 0.06$ mm, monoclinic, $P2_1/c$, $a = 15.471(2)$, $b = 29.281(1)$, $c = 26.472(2)$ Å, $\beta = 103.64(1)°$, $V = 11\,653(2)$ Å^3, $Z = 4$, $\rho_{calcd} = 1.938\ g\,cm^{-3}$, $\theta = 1.86–25.15°$, $\mu = 3.329\ mm^{-1}$, 32 866 measured reflections, 16 178 independent reflections ($R_{int} = 0.122$), 3384 observed reflections ($I > 2\sigma(I)$), 614 refined parameters, $R1 = 0.0593$, $wR2 = 0.0912$, max./min. residual electron density $0.701/-0.558\ e\,Å^{-3}$. Data were collected on a STOE-IPDS diffractometer ($Mo_{K\alpha}$ radiation) at 173 K. The structure was solved by direct methods using SIR97 and refined against F^2 (SHELXL-97) with all reflections. Refinement with anisotropic temperature factors was only possible for the heavy atoms. Remaining, still important residual electron densities from the difference Fourier analyses could not be refined. Voids at $x, y, z = 0.5, 0.0, 0.5$ and $x, y, z = 0.5, 0.5, 0.0$ were localized with the program SQUEEZE.[14] Each of them has a volume of 1281 Å^3 and contains 48 and 49 electrons, respectively. These numbers correspond roughly to toluene molecules, however, the volume of the voids is too high for only one such molecule. The portion of these electrons at the calculated structure factors was considered by Fourier back transformation and was subtracted from the observed structure factors. The final refinement was carried out with these data. Crystallographic data (excluding structure factors) for the structure reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication no. CCDC-155021. Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB21EZ, UK (fax: (+44)1223-336-033; e-mail: deposit@ccdc.cam.ac.uk).

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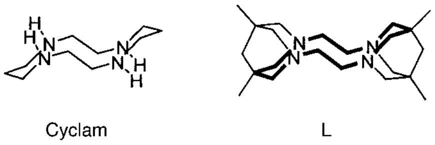
A Very Rigid Bis-bispidine Tetraazamacrocycle and Its Unusual Copper(II) Complex[**]

Peter Comba,* Hans Pritzkow, and Wolfgang Schiek

Dedicated to Professor Dieter Sellmann
on the occasion of his 60th birthday

Macrocyclic ligands have been used extensively to stabilize metal ions in specific oxidation and electronic states, and to tune the metal ion selectivity.[1–5] The 14-membered tetraazamacrocycle cyclam (1,4,8,11-tetraazacyclotetradecane; Scheme 1) is known to provide an ideal donor set and geometry for tetragonal coordination of copper(II) centers.



Scheme 1. The ligands cyclam and L (=**3**).

The conformational flexibility of the five- and six-membered chelate rings and the configurational flexibility of the coordinated secondary amino groups of cyclam and other tetraazamacrocyclic ligands may be reduced and, therefore, the selectivity increased by substituents at the amines or the carbon backbone or by reinforcing the backbone with rings or multiple bonds.[6–8] Several attempts have been made to decrease the flexibility of the cyclam backbone, for example, with derivatives containing one or two piperazine rings.[9, 10] The bispidine backbone (bispidine = 3,7-diazabicyclo[3.3.1]-nonane) is known to be an extremely rigid fragment, and a range of *N*,*N*′-substituted tetradentate,[11, 12] as well as C^{α},$C^{\alpha'}$-substituted tetra-,[13–18] penta-, and hexadentate ligands,[18] and their transition metal compounds have been prepared and studied. Macrocyclic cyclam derivatives with two bispidine caps are expected to be highly preorganized and extremely rigid. These ligands have no configurational flexibility; with respect to the conformation there are only two possible arrangements of the five-membered chelate rings: λ,λ and λ,δ.

Derivatives of L have been proposed and reported but neither a full characterization, including an experimental structure, nor any spectroscopically or structurally characterized metal complexes have been published.[19, 20]

Molecular models of the free ligand L and the corresponding copper(II) compound (two conformations each) are shown in Figure 1.[21–25] These indicate that, indeed, L is highly preorganized for coordination of copper(II). The only distortions are a zigzag orientation for the λ,δ conformer and a twist of the two planes defined by the two N donors and the central carbon atom of the methylene bridge of each bispidine cap for the λ,λ conformer. These distortions arise due to the

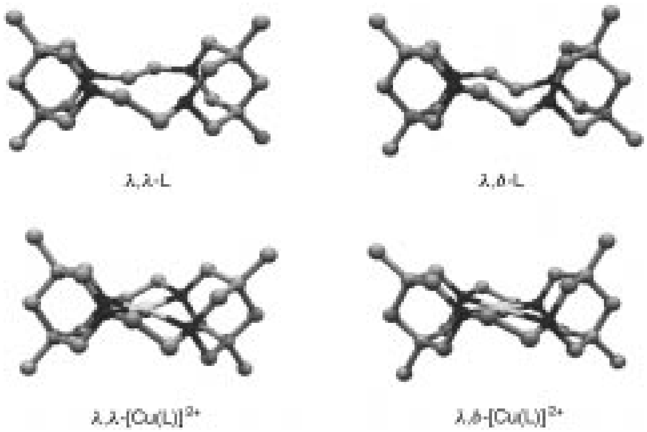


Figure 1. Computed structures of L and $[Cu(L)]^{2+}$.[21–23]

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