Acetylenedithiolate: alkyne complex formation renders it a dithiolate chelate ligand†

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The isostructural complexes [{Tp′W(CO)$_2$(η^2-C$_2$S$_2$)}$_2$M] (M = Ni, Pd, Pt) show that the η^2-*C*,*C*′-alkyne complexes of acetylenedithiolate at [Tp′W(CO)$_2$]$^+$ can generally act as dithiolate chelate ligands, leading to dithiolene type complexes.

Recently we reported a bimetallic tungsten–ruthenium complex exhibiting an unprecedented μ-η^2-*C*,*C*′-η^2-*S*,*S*′ bridging mode of acetylenedithiolate.[1] The synthetic approach comprises of the preparation of the alkyne complex [Tp′W(CO)$_2${η^2-(BnS)CC(SBn)}](PF$_6$), successive[2] reductive removal of the benzyl groups at the sulfur atoms and finally the reaction of K[Tp′W(CO)$_2$(η^2-C$_2$S$_2$)] (K–**1**) with [(η^5-C$_5$H$_5$)Ru(PPh$_3$)(CH$_3$CN)$_2$] (PF$_6$).[1] Since the product [Tp′W(CO)$_2$(C$_2$S$_2$)Ru(η^5-C$_5$H$_5$)(PPh$_3$)] shows structural similarities-to and properties-of dithiolene complexes, we have been interested in the question of whether the mono-anionic acetylenedithiolate complex [Tp′W(CO)$_2$(η^2-C$_2$S$_2$)]$^-$ (**1**$^-$) can generally be used as dithiolate chelate ligand. In particular, we have pursued homoleptic complexes of **1**$^-$, in analogy to classical dithiolene complexes. Herein, we report on the isostructural complexes [M(**1**)$_2$] (M = Ni, Pd, Pt), proving the fact that the *S*,*S*′-chelate coordination of **1**$^-$ is not restricted to particular (steric or electronic) requirements of the *S*,*S*′-bound complex moiety.

Reaction of two equivalents of K[Tp′W(CO)$_2$(η^2-C$_2$S$_2$)] (K–**1**) with [Ni(NCMe)$_6$](BF$_4$)$_2$ and [PtCl$_2$(NCPh)$_2$], respectively, in THF lead to blue solutions. Surprisingly, the palladium congener [Pd(NCMe)$_4$](BF$_4$)$_2$ yielded a red solution under the same reaction conditions. In all cases, complex formation was indicated by an increase in the stretching frequencies of the tungsten-bound CO ligands ($\Delta\tilde{\nu}$ = 33 and 50 cm^{-1}). The complexes [Ni(**1**)$_2$] **2**, [Pd(**1**)$_2$] **3** and [Pt(**1**)$_2$] **4** were obtained analytically pure after column chromatography and direct crystallization from the eluted toluene solutions.‡ The crystals of **2**, **3** and **4** were isomorphous, revealing similarities in their overall molecular structure (Fig. 1 and Table 1).§ The central metal ions, which lie on an inversion center, are coordinated by two **1**$^-$ metalla-ligands in a square-planar fashion. The bend-back of the sulfur substituents in the tungsten–alkyne complex moieties is remarkably large, which allows chelate coordination of both sulfur atoms to the central metal ion. The bend-back angles in four-electron donor alkyne complexes usually amount to about 140°.[3] Therefore, the observed bend-back angles (120.7° and 125.3° in **2**) are forced by the apparently favoured chelate ring formation. Consequently, the bend-back angles in the **1**$^-$ dithioalkyne complexes are rather flexible. The chelate rings are both planar and are co-planar to each other. The symmetry of the single WC$_2$S$_2$M chelate rings is evident by comparison of the bond lengths M–S1, S1–C1 and C1–W with M–S2, S2–C2 and C2–W, respectively. In fact, the sulfur coordination in **2**, **3** and **4** adopts a typical dithiolene structure.

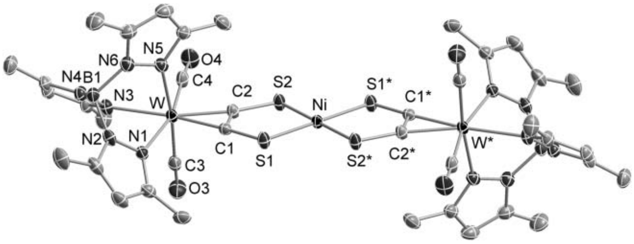

Fig. 1 Molecular structure of **2**. H atoms have been omitted for clarity. The ellipsoids are drawn at 50% probability.

However, the M–S bonds lengths are strikingly long compared to the corresponding neutral dithiolene complexes.[4] This observation is particularly evident for the nickel system. While typical Ni–S bond lengths in neutral square-planar four-coordinated sulfur complexes amount to 2.128 Å in [Ni(S$_2$C$_2$Me$_2$)$_2$],[5] 2.126 Å in [Ni(S$_2$C$_6$H$_2{}^t$Bu$_2$)$_2$],[6] 2.156 Å in [Ni(dithioacetylacetonate)$_2$][7] and 2.161 Å in [Ni{(S)(SMe)C$_2$Ph$_2$}$_2$],[8] the Ni–S bond lengths in **2** are distinctively longer (Ni–S1 2.211 Å and Ni–S2 2.214 Å). With respect to the Ni–S bond lengths, complex **2** is comparable with the nickelbis(dithiosquarate) complex K$_2$[Ni(S$_2$C$_4$O$_2$)$_2$],[9] for which such Ni–S bonds are rather expected due to its dianionic nature.

Recent comprehensive re-evaluation of the electronic structures of nickelbis(ethylenedithiolate)[5] and metalbis(benzenedithiolate) (M = Ni, Pd, Pt)[10] complexes have shown that the diamagnetic neutral compounds consist of divalent metal centers (nd^8, S_M = 0)

Table 1 Selected bond lengths (Å) and angles (°) in **2**, **3** and **4**[a]

	Ni (**2**)	Pd (**3**)	Pt (**4**)
M–S1	2.2112(12)	2.3384(12)	2.3180(15)
M–S2	2.2145(12)	2.3416(12)	2.3176(15)
C1–S1	1.682(5)	1.698(4)	1.695(6)
C2–S2	1.680(5)	1.701(4)	1.700(6)
C1–C2	1.373(6)	1.360(6)	1.358(8)
W–C1	2.024(5)	2.026(4)	2.017(5)
W–C2	2.043(4)	2.042(4)	2.032(6)
C1–C2–S2	125.3(4)	127.2(3)	126.4(5)
C2–C1–S1	120.7(3)	123.6(3)	122.1(4)
S1–M–S2	92.84(4)	90.76(4)	89.73(5)
S1–M–S2*	87.16(4)	89.24(4)	90.27(5)

[a] Symmetry transformations used to generate equivalent atoms: $-x + 1$, $-y + 1$, $-z + 1$.

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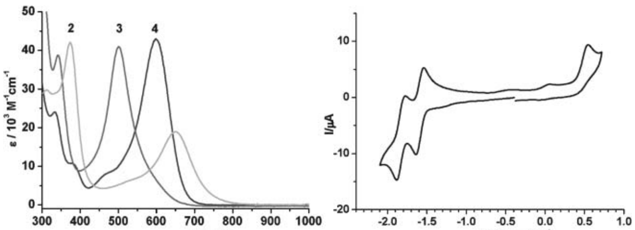
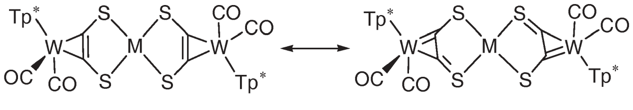


Fig. 2 Left: UV/vis spectra of **2**, **3** and **4** in CH_2Cl_2. Right: Cyclic voltammogram of **3** in CH_2Cl_2.

and two *S*,*S*′-coordinated dithio(1^-) π-radical anions. The two spins are antiferromagnetically coupled *via* a superexchange mechanism mediated through the diamagnetic metal(II) ion. Accordingly, the oxidation state II is assigned to the central metal in **2**, **3** and **4**. As indicated by the resonance structures **A** and **B**, a radical formulation is not necessary in **2**, **3** and **4** due to the electronic conjugation to tungsten. This difference in the electronic structure compared to dithiolene complexes is reflected in their UV/vis spectra. Complexes with 1,2-dithiosemiquinonate(1^-) π-radical anions consistently show an intense band between 800 and 900 nm, which varies little upon exchange of the central metal ion.[10] These transitions are consequently assigned to a ligand-to-ligand charge transfer. Likewise, complexes **2**, **3** and **4** exhibit an intense band in the visible range of the spectra (Fig. 2). However, this transition is remarkably shifted upon exchange of the central metal ion in the order Ni (649 nm), Pt (599 nm) and Pd (501 nm), rendering a solution of **3** already red-coloured. This observation indicates a significant contribution of the central metal d-orbitals in the transition.



A **B**

Cyclic voltammetry showed two reversible one-electron transfer waves for **2**, **3** and **4** (Fig. 2). The potentials are nearly independent of the nature of the central metal ion for both electron transfers, respectively. The potentials of the first transfer ($E_{1/2}$ *vs.* Fc/Fc^+) amount to −1.54 V for **2**, −1.59 V for **3** and −1.56 V for **4**. Therefore, both redox processes are assigned to the tungsten–alkyne complex moiety. This conclusion is proven by the stoichiometric reduction of **3** with sodium naphthalide. The one-electron reduction of **3**, which is also chemically reversible, affects a shift of both CO stretching frequencies by 35 and 48 cm^{-1} respectively. The observation of only two shifted CO bands is consistent with reduced mixed-valence tungsten centers of class III, according to the classification of Robin and Day.[11] The average difference of 250 mV between the first and second electron transfer proves the electronic cooperativity of both tungsten centers over the central metal ion. However, this difference is much smaller compared to classical dithiolene complexes (ΔE = 900 mV for $[Ni(S_2C_2Me_2)_2]^5$), reflecting the larger distance between the redox active centers compared to dithiolene complexes, with high single electron densities at their sulfur atoms.

Interestingly, the nickel complex **2** reacts easily with neutral donors like acetonitrile or pyridine to yield yellow solutions, in which the strong visible band at 649 nm is quenched. The magnetic moment of $\mu_{eff} = 3.28\mu_B$ of the solved species, as estimated by the Evans method, points to an octahedral complex $[Ni(\mathbf{1})_2L_2]$ (L = pyridine). The coordination of pyridine turns out to be reversible because, after removal of the solvents *in vacuo*, **2** was recovered in pure dichloromethane.

In this contribution we have shown that the monoanionic acetylenedithiolate complex $[Tp'W(CO)_2(\eta^2\text{-}C_2S_2)]^-$ ($\mathbf{1}^-$) is capable of forming square planar bis-complexes with group 10 metal ions. The combination of the sulfur donors and their conjugation to the alkyne-bound metal center renders the monoanionic dithiolate ligand $\mathbf{1}^-$ highly polarizable and "soft". The withdrawal of electron density from the tungsten, as a consequence of the coordination of a metal ion at the sulfur atoms, is evident from the increase in the CO stretching frequencies. The strong cooperativity of the three metal centers in the complexes presented here is reflected in their electronic spectra and electrochemical data.

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Notes and references

‡ *Selected spectral data for the complexes*. **4**: Anal. calc. for **4**·2 toluene ($C_{52}H_{60}B_2N_{12}O_4S_4PtW_2$): C, 38.32; H, 3.71; N, 10.31. Found: C, 38.33; H, 3.75; N, 10.21%. IR (KBr) (cm^{-1}): ṽ = 2009 (s, CO) and 1956 (s, CO). ^1H NMR (CD_2Cl_2, 400 MHz, 298 K): δ = 5.94 (s, 1 H, C*H*($CCH_3)_2$), 5.92 (s, 2 H, C*H*($CCH_3)_2$), 2.52 (s, 3 H, CC*H*$_3$), 2.40 (s, 6 H, CC*H*$_3$), 2.34 (s, 3 H, CC*H*$_3$) and 2.21 (s, 6 H, CC*H*$_3$). ^{13}C NMR (CD_2Cl_2, 100.6 MHz, 298 K): δ = 215.7 (W*C*O), 154.2, 153.7, 147.3, 145.3 (CH(*C*CH$_3$)$_2$), 108.3, 107.5 (*C*H($CCH_3)_2$), 15.8, 15.0, 12.6 and 12.3 (C*C*H$_3$). The alkyne resonances are coalesced).

§ *Crystal data*: **2**·2 C_7H_8: $C_{52}H_{60}B_2N_{12}NiO_4S_4W_2$, *M* = 1493.39, monoclinic, space group *P*2(1)/*n*, *a* = 10.1411(17), *b* = 18.928(3), *c* = 15.605(3) Å, *β* = 101.751(3), *Z* = 2, *U* = 2932.6(8) Å^3, *μ*(Mo-Kα) = 4.427 mm^{-1}, *T* = 153 K, 33188 reflections collected, 8547 unique (R_{int} = 0.0593), wR_2 (all data) = 0.0994, CCDC 610641. **3**·2 C_7H_8: $C_{52}H_{60}B_2N_{12}PdO_4S_4W_2$, *M* = 1541.08, monoclinic, space group *P*2(1)/*n*, *a* = 10.1900(17), *b* = 18.993(3), *c* = 15.757(3) Å, *β* = 101.582(3), *Z* = 2, *U* = 2987.4(9) Å^3, *μ*(Mo-Kα) = 4.332 mm^{-1}, *T* = 153 K, 28696 reflections collected, 6859 unique (R_{int} = 0.0626), wR_2 (all data) = 0.0734, CCDC 610641. **4**·2 C_7H_8: $C_{52}H_{60}B_2N_{12}PtO_4S_4W_2$, *M* = 1629.77, monoclinic, space group *P*2(1)/*n*, *a* = 10.1525(13), *b* = 18.891(3), *c* = 15.748(2) Å, *β* = 101.498(3), *Z* = 2, *U* = 2959.6(7) Å^3, *μ*(Mo-Kα) = 6.429 mm^{-1}, *T* = 153 K, 28647 reflections collected, 6793 unique (R_{int} = 0.0521), wR_2 (all data) = 0.0911, CCDC 610643. For crystallographic data in CIF or other electronic format see DOI: 10.1039/b606068d.

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