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Preliminary Communication

Rigidity of the unsymmetric coordination geometry of the two dithiolates in $(C_5Me_5)Ta(norbornane\text{-}exo\text{-}2,3\text{-}dithiolate)_2$

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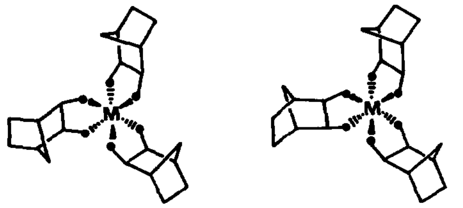
Abstract

We have synthesized $(C_5Me_5)Ta(norbornane\text{-}exo\text{-}2,3\text{-}dithiolate)_2$ and found that the two dithiolate ligands coordinate to Ta with opposite orientations with respect to Cp*. In the ^1H NMR time scale, this unique geometry is rigid up to 100°C.

In the course of our study on the homoleptic dithiolate complexes of Group 5 metals [1–3], we found that $[A][M(ndt)_3]$ ($A = Et_4N^+$, $(^nBu)_4N^+$, Ph_4P^+; M = Nb, Ta; ndt = norbornane-exo-2,3-dithiolate) had two unusual geometrical isomers, *synclastic* **I** and *anticlastic* **II** (Scheme 1), and they underwent facile interconversion in solution [4]. The kinetic data for the isomerization suggested polytopal rearrangement pathways without M–S bond rupture. In order to gain further insight into the behavior of such a dithiolate ligand at the Group 5 metal center, we synthesized a closely related bis-ndt complex, $Cp^*Ta(ndt)_2$ ($Cp^* = C_5Me_5$) (**1**), which is the focus of this paper. Also, this is an outgrowth of our continuing interests in half-sandwich complexes of tantalum having *S*-donor ligands [5–7].

When a solution of Cp^*TaCl_4 in THF was added dropwise to a solution of 2 equiv. of $Li_2(ndt)$ in THF, a dark brown color developed immediately. Evaporation of the solvent, extraction of the solid with hexane, and recrystallization from hexane/THF afforded **1** as deep green microcrystals in 41% yield [8*]. The complex **1** is air/moisture sensitive, but thermally stable up to *ca.* 180°C in the solid state. In the ^1H NMR (400 MHz, C_6D_6) spectra, illustrated in Fig. 1, there appear two sets of peaks arising from the ndt protons, which were fully assigned based on a series of decoupling procedures and the NOE measurements (Cp* protons *vs.* H1). Their chemical shifts are compared with those of $[Ph_4P][Ta(ndt)_3]$ [4] and H_2ndt in Table 1.



Synclastic **Anticlastic**

I II

Scheme 1.

Non-equivalence of the two ndt ligands in **1** is consistent with the structure **III** in Scheme 2 (top) in which the methylene bridge of ndt-A points away from the Cp* ring and that of ndt-B adopts the opposite orientation. Interestingly, the H1 doublet moves to downfield relative to the corresponding H_2ndt signal, significantly so for ndt-B. On the other hand, a large downfield shift of the H5 resonance was observed for ndt-A. The ring-current effects of Cp* must be responsible for these phenomena.

The interesting geometry of **1** may be relevant to the unsymmetrical folding of two ethylene-*cis*-1,2-dithiolate (edt) ligands observed for $Cp^*Ta(edt)_2$ (**2**) [5], *i.e.*, structure **IV** shown in Scheme 2 (bottom). This coordination mode was rationalized in terms of the maximum bonding interactions between C=C π orbitals of edt and the two low-lying vacant d orbitals of Ta. The two identical conformers, **IV** and **IV′**, are in equilibrium ($\Delta G_{50°C} = 14.9$ kcal mol^{-1}) in solution, probably *via* an inversion process of the TaS_2C_2 chelate rings. Such a process does not equilibrate the two ndt ligands in **1**, because the non-equivalence originates from the unsymmetric nature of ndt itself imposed on the direction perpendicular to the TaS_2 plane. Having a sizeable Cp* ligand, complex **1** is also unlikely to undergo polytopal rearrangements because of steric reasons. In

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* Reference number with asterisk indicates a note in the list of references.

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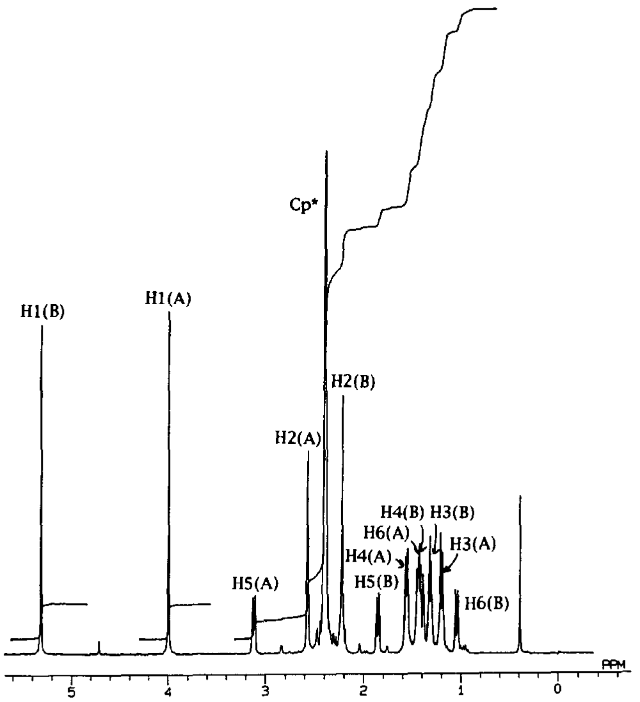
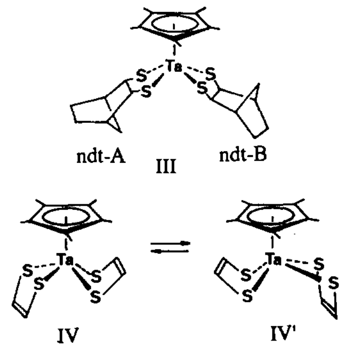


Fig. 1. 400 MHz ^1H NMR spectrum (ppm/δ) of $Cp^*Ta(ndt)_2$ (**1**) in C_6D_6. Note that multiplicity of each resonance is masked in the small-scale chart, and the details along with the numbering scheme are given in Table 1.

fact, the spectral pattern of Fig. 1 remains unchanged up to 100°C in toluene-d_8.

If the ndt ligands in **1** would be fluxional, then a possible pathway could be the one involving Ta–S bond rupture, which should be a high energy process according to the temperature independence of the ^1H NMR up to 100°C. Suppose that the H3 signals coalesce at 100°C [9*], then the calculated barrier to the pathway could be 19 kcal mol^{-1}. Since we did not observe even a sign of broadening of these peaks, the activation energy must be much higher. The rigidity of the ndt coordination in **1** provides a firmer footing for the non-bond-rupture mechanisms proposed for the facile **I** ⇄ **II** rearrangement of [A][M(ndt)$_3$] (M = Nb, Ta) ($\Delta G_{30^\circ C}$ = 12.6–13.7 kcal mol^{-1}) and for the **IV** ⇄ **IV′** equilibration of **2**.



Scheme 2.

It should be noted here that the EI fragmentation of **1** consists of signals derived from $Cp^*Ta(S_2)(ndt)^+$ and $Cp^*Ta(S_2)_2{}^+$ in addition to the parent ion isotopic cluster. This is analogous to the stepwise liberation of ethylene portions in the EI fragmentation pattern of **2**, suggesting that C–S bonds of the alkanedithiolates are cleaved cleanly in the EI mass condition.

References and notes

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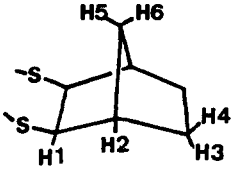
TABLE 1. Comparison of 400 MHz ^1H NMR data for the ndt protons of $Cp^*Ta(ndt)_2$ (**1**), [Ph_4P][Ta(ndt)$_3$] and H_2ndt [a]



^1H NMR	Chemical shift, ppm						Coupling constant, Hz		
	H1	H2	H3	H4	H5	H6	J(H1H6)	J(H3H5)	J(H5H6)
1 (ndt-A) [b]	3.99(d)	2.59(dt)	1.13(m)	1.47(m)	3.16(dt)	1.38(dt)	1.71	2.08	9.64
1 (ndt-B) [b]	5.36(d)	2.39(dt)	1.23(m)	1.34(m)	1.88(dt)	1.00(dt)	1.95	2.08	9.64
[Ph_4P][Ta(ndt)$_3$] [c]	4.03(s, br)	2.09(m)	1.06(m)	1.37(m)	2.46(s, br)	0.92(d, br)	(2) [e]	(2) [e]	9.5
H_2ndt [d]	3.24(m)	2.25(m)	1.29(m)	1.60(m)	1.95(dt)	1.18(dt)	1.5	1.8	10.4

[a] Ppm downfield from TMS, room temperature. [b] In C_6D_6. [c] In CD_2Cl_2. [d] in $CDCl_3$. [e] Estimated from the 100 MHz ^1H NMR in CD_3CN.

3 For other homoleptic dithiolate complexes of Ta and Nb, see: (a) M. J. Bennett, M. Cowie, J. L. Martin and J. Takats, *J. Am. Chem. Soc.*, *95* (1973) 7504; (b) M. Cowie and M. J. Bennett, *Inorg. Chem.*, *15* (1976) 1584, 1589, and 1595.

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8 Cp*Ta(ndt)$_2$, deep green microcrystals, m.p. 200–202°C (dec.). UV/VIS ($\lambda_{max}(\epsilon)$, THF, nm) 271(2700), 323(2200), 384(1900), 600 br (400). far-IR (Nujol mull, cm^{-1}): 399 s, 386 s, 371 m, 360 s, 348 m, 334 m. MS (EI, 70 eV, m/e) 632 (Cp*Ta(ndt)$_2$+), 538 (Cp*Ta(S$_2$)(ndt)$^+$), 444 (Cp*Ta(S$_2$)$_2$+). Anal. Found: C, 45.28, H, 5.60; S, 20.10; Ta, 28.93. $C_{24}H_{35}S_4Ta$ calcd.: C, 45.56; H, 5.58; S, 20.27; Ta, 28.60%.

9 The difference in ^{1}H chemical shifts between ndt-A and ndt-B is smallest for H3.