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Unusual reactivity of tantalum pentakis(dimethylpyrazolate) with CS_2: scission of the C=S bond and formation of $dmpz_3CS^-$ ligand

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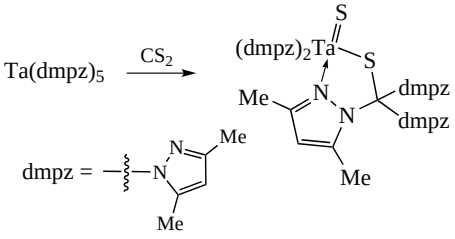
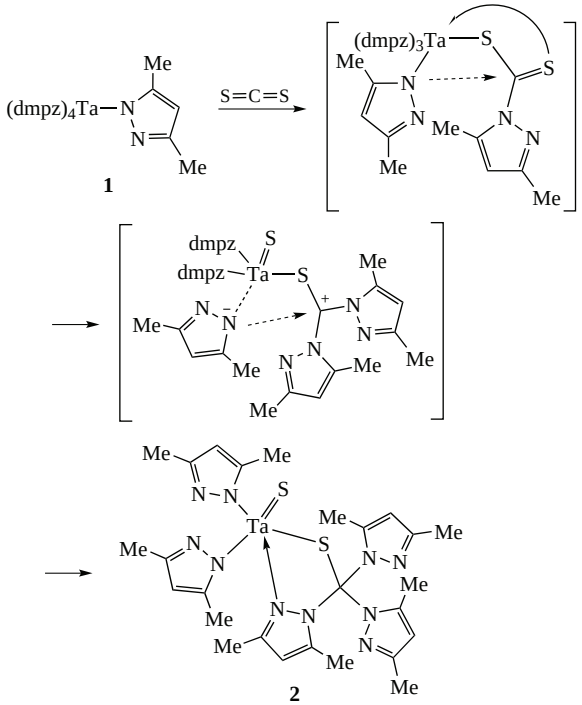
The reaction beetwen tantalum pentakis(3,5-dimethylpyrazolate) and CS_2 afforded novel complex $[Ta(=S)(dmpz)_2\{(dmpz)_3CS\}]$. In this reaction the molecule of CS_2 undergoes scission with the migration of one sulfide to the tantalum atom while three pyrazolate residues migrate to carbon with the formation of unusual $(dmpz)_3CS^-$ ligand. The structure of the product was established by X-ray diffraction.



Keywords: tantalum complexes, amides, pyrazolates, sulfides, carbon disulfide, dithiocarbamates.

Metal amides are key compounds in modern coordination chemistry and are convenient precursor complexes due to the basic, nucleophilic, and reducing properties of amide groups.[1–3] For instance, insertion of CS_2 into polar M–N bonds is a common method for the synthesis of dithiocarbamates of early transition metals from their amides.[4,5] The reaction of $[Nb(NMe_2)_5]$ with CS_2 leads to a complex of tetravalent niobium $[Nb^{IV}(^{Me}dtc)_4]$ and 0.5 equiv. of $(^{Me}dtc)_2$.[5] A similar reaction of $Ta(NMe_2)_5$ results in the $Ta(^{Me}dtc)_5$ product, which was thought to have the molecular structure ($[Ta(\eta^2\text{-}^{Me}dtc)_3(\eta^1\text{-}^{Me}dtc)_2]$) with different coordination of dithiocarbamate.[6] Nevertheless, as we found, the structure of the product corresponded to the ionic compound $[Ta(^{Me}dtc)_4](^{Me}dtc)$.[7] The reaction of $Ta(NMe_2)_5$ and CS_2 in a ratio of 1 : 3 leads to product $[Ta(^{Me}dtc)_3(CH_2NMe)]$ with the dianionic ligand $\eta^2\text{-}CH_2NMe^{2-}$ which provides a Ta–C bond.[8] It seems interesting to study the reactions of CS_2 and other heterocumulenes with heterocyclic amides of early transition metals, in particular, pyrazolates. Pyrazole-based dithiocarbamates are rare[9–15] and completely unknown for early transition metals. In this work, we aimed to study the reaction of $[Ta(dmpz)_5]$ **1** with CS_2 (Scheme 1).

The reaction of compound **1**[16] with an excess of CS_2 and recrystallization of the product from toluene led to the formation of yellow crystals.† Based on X-ray diffraction analysis, the formula $[TaS(dmpz)_2\{(dmpz)_3CS\}]\cdot 0.5\,C_7H_8$ (**2**$\cdot 0.5C_7H_8$)



Scheme 1 *Reagents and conditions*: i, toluene, 60 °C, 18 h.

† *Synthesis of bis(*N,N′*-3,5-dimethylpyrazolato)(*N,S-*tris(3,5-dimethyl-1-pyrazolyl)methylthiolato)sulfidotantalum(V) [TaS(dmpz)$_2${(dmpz)$_3$SC}]* **2**. Compound $Ta(dmpz)_5$ (117 mg, 0.178 mmol) was placed in a Schlenk flask, evacuated, cooled to –196 °C, and toluene (15 ml) and CS_2 (300 μl, 3.13 mmol) were vacuum-transferred. The mixture was warmed to room temperature and heated at 60 °C for 18 h. The orange solution was cooled to room temperature and evaporated to dryness *in vacuo*. The residue was extracted with toluene, the extract was placed in a two-legged ampoule and sealed. Slow evaporation of the solvent caused formation of orange crystals **2**$\cdot 0.5\,C_7H_8$ suitable for XRD. Yield 70 mg (67%). ^{1}H NMR (C_6D_6): δ 1.55 (s, 3H, CH_3), 1.62 (s, 3H, CH_3), 1.88 (br. s, 3H, CH_3), 2.05 (br. s, 6H, CH_3), 2.11 (br. s, 3H, CH_3), 2.21 (br. s, 6H, CH_3), 2.47 (br. s, 3H, CH_3), 2.97 (br. s, 3H, CH_3), 5.23 (s, 1H, CH), 5.85 (s, 2H, CH), 6.28 (s, 2H, CH). ^{13}C{^{1}H} NMR (C_6D_6): δ 11.5, 12.5, 13.1, 13.8, 14.1, 14.4, 16.7, 100.5 (SCN_3), 109.8, 110.6, 115.7, 116.7, 140.9, 144.6, 145.6, 146.5, 147.5, 148.2, 148.9, 150.0. ^{15}N NMR (C_6D_6): δ 219, 261. IR (KBr, ν/cm^{-1}): 2925, 1563, 1525, 1413, 1370, 1334, 1239, 1218, 1133, 1032, 1009, 981, 959, 909, 864, 825, 786, 768, 729, 715, 636, 586. Found (%): C, 42.30; H, 4.90; N, 19.25. Calc. for $C_{26}H_{35}N_{10}S_2Ta$ (%): C, 42.62; H, 4.81; N, 19.12. Extraction of the reaction product with C_6H_6 yielded, after similar work-up, single crystals of the solvatomorph **2**$\cdot 0.5\,C_6H_6$, which was characterized by X-ray analysis.

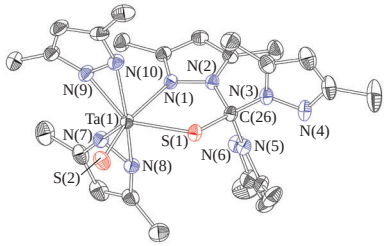


Figure 1 Crystal structure of complex **2** (thermal ellipsoids of 30% probability, H atoms are omitted for clarity).

was assigned to them (Figure 1). Despite the excess of CS_2 used, only one equivalent reacts with the initial complex **1**. Apparently, the introduction of one CS_2 molecule leads to steric overload of the coordination site, which makes the C–S bond to break and provides the migration of two dimethylpyrazolate groups from Ta to C (see Scheme 1). As a result, a complex with a novel scorpionate-like ligand $(dmpz)_3CS^-$ is formed. Molecular geometry analysis using the Shape program[17,18] indicates a pentagonal bipyramid as the coordination polyhedron [S_Q(PBP) = 7.039], although the S_Q value for a capped trigonal prism is close [S_Q(CTP) = 8.822]. The axial positions in the PBP are occupied by the S(2) and N(1) atoms; the S(2)–Ta(1)–N(1) angle [163.38(6)°] differs significantly from the ideal 180°. The Ta=S distance [2.1888(9)Å], as well as the chelate angles of the pyrazolate ligands, are close to those in the previously described complexes. The planes of two pyrazolate ligands are close to the equatorial plane of the coordination polyhedron; the angle between them is 22.8°. Of the three pyrazolate substituents of the $(dmpz)_3CS^-$ ligand, only one is coordinated to Ta; the angle between the planes of the other two is 64.9°. Another similar solvate **2**·0.5C_6H_6 was obtained after recrystallization of the reaction mixture form benzene. The geometric characteristics of complex **2** in both solvates are close (Table 1). The TaS_2N_5 coordination polyhedron, according to the analysis using the Shape program, is also best described by a pentagonal bipyramid [S_Q(PBP) = 7.023].‡

An interesting feature of complex **2** is the presence of a quaternary carbon atom, the environment of which does not contain other carbon atoms. Such compounds are quite rare in organic and coordination chemistry. Examples of tetrasubstituted methane derivatives include compounds of the type CX_4 (X = halogen, N_3,[19] amide[20–23]) and $XC(NO_2)_3$ (X = halogen,[24,25] N_3 [26]). A few complexes with the ligands of type $\{Pz_3CX\}^n$ (n = 0, –1), in which the tris(pyrazolyl)methyl fragment is coordinated to heteroatomic group (X = PR_2,[27] SO_3^-,[28,29] RS[30,31]) are also known. Complex **1** uniquely differs in that the $(dmpz)_3CS^-$ ligand is formed directly in the coordination sphere of metal. The structures of two salts containing the pz_3CS^- anion, a derivative of unsubstituted pyrazole, have also been published.[30] Their main difference is the significantly longer C–S bonds [1.778(4) and 1.788(3) Å] compared to those in **2**.

Table 1 Principal bond lengths (Å) and angles (°) in solvates **2**·0.5C_7H_8 and **2**·0.5C_6H_6.

Parameter	**2**·0.5C_7H_8	**2**·0.5C_6H_6
Ta(1)–S(1)	2.4441(8)	2.4489(18)
Ta(1)–S(2)	2.1888(9)	2.1898(18)
Ta(1)–N(1)	2.331(2)	2.351(5)
Ta(1)–N(7)	2.100(3)	2.138(6)
Ta(1)–N(8)	2.097(3)	2.084(6)
Ta(1)–N(9)	2.068(3)	2.079(5)
Ta(1)–N(10)	2.218(3)	2.169(6)
S(1)–C(26)	1.839(3)	1.838(7)
N(7)–Ta(1)–N(8)	38.06(10)	38.2(2)
N(9)–Ta(1)–N(10)	37.31(10)	38.0(2)
Ta(1)–S(1)–C(26)	105.59(10)	107.1(2)

It is worth noting than activation of CS_2 by metal complexes can proceed in different ways. In many cases the CS_2 moiety is preserved, and oxidative addition (to give η_2-CS_2 complexes)[32] or insertion into M–X (X = OR, NR_2, SR) bonds to give $M(S_2CX)$ moieties are observed.[33] Scission of the C=S bond in CS_2 was observed in the reactions with highly reactive silylenes[34] and aluminum hydrides.[35] This bond can also be cleaved by uranium(VI) nitride complexes with the formation of NCS^- and S; U^{VI} having been reduced to U^{IV}.[36] Our case is remarkable insofar it does not involve redox transformation but rather exchange of S and pyrazolates between Ta and C. Last but not the least, reactivity studies of CS_2 with metal complexes may have biomedical relevance.[33]

Solution ^{1}H and ^{13}C NMR data are in agreement with the crystal structure of **2**. The spectra show signals corresponding to six single and two paired methyl groups. In the aromatic region, three signals from CH groups with a mutual ratio of 2:2:1 are detected. In solution, the molecule exhibits stereochemical nonrigidity: the signals of the terminal dimethylpyrazole fragments are significantly broadened in both ^{1}H and ^{13}C NMR spectra. In the ^{1}H NMR spectrum, the half-width of the signals from methyl groups is 25–37 Hz. As a result, two-dimensional correlation spectroscopy cannot unambiguously assign the signals of terminal pyrazoles. On the other hand, the stereochemical rigidity of the pyrazole fragment, which participates in the five-membered TaNNCS metallocycle, made it possible to completely identify the ^{1}H and ^{13}C signals related to it, as well as to obtain information on the chemical shifts of nitrogen atoms when δ(^{15}N) is 219 and 261 for the N(1) and N(2) atoms, respectively. The chemical shifts of the remaining N atoms could not be observed.

‡ *Crystal data for* **2**·0.5C_7H_8. $C_{29.5}H_{39}N_{10}S_2Ta$, M = 778.77 g mol^{-1}, monoclinic, space group $P2_1/c$ (no. 14), a = 23.9350(5) Å, b = 9.1814(2) Å, c = 15.7189(3) Å, β = 99.8460(10)°, V = 3403.46(12) Å^3, Z = 4, μ = 3.388 mm^{-1}, d_{calc} = 1.520 g cm^{-3}, 83586 reflections measured (4.616° ⩽ 2θ ⩽ 55.756°), 10123 unique (R_{int} = 0.0501, R_{sigma} = 0.0286) which were used in all calculations. The final R_1 was 0.0301 [$I > 2\sigma(I)$] and wR_2 was 0.0704 (all data). GOOF = 1.043, largest diff. peak/hole 0.86/–0.87 eÅ^{-3}.

Crystal data for **2**·0.5C_6H_6. $C_{29}H_{38}N_{10}S_2Ta$, M = 771.76 g mol^{-1}, triclinic, space group $P\bar{1}$ (no. 2), a = 8.7874(5) Å, b = 14.0656(9) Å, c = 14.7844(11) Å, α = 113.526(2)°, β = 90.039(2)°, γ = 103.481(2)°, V = 1620.27(19) Å^3, Z = 2, μ = 3.557 mm^{-1}, d_{calc} = 1.582 g cm^{-3}, 17456 reflections measured (3.266° ⩽ 2θ ⩽ 53.216°), 6655 unique (R_{int} = 0.1079, R_{sigma} = 0.0698) which were used in all calculations. The final R_1 was 0.0490 [$I > 2\sigma(I)$] and wR_2 was 0.1016 (all data). GOOF = 0.961, largest diff. peak/hole 1.61/–1.23 eÅ^{-3}.

The XRD analysis of **2**·0.5C_7H_8 was performed on a Bruker D8 Venture diffractometer with CMOS PHOTON III detector. The data collection for **2**·0.5C_6H_6 was run on a Bruker Duo diffractometer equipped with a 4K CCD area detector. Graphite-monochromated MoKα radiation (λ = 0.71073 Å) was used. The φ- and ω-scan techniques were employed to measure diffraction intensities. Absorption corrections were applied with the use of the SADABS program.[37] The crystal structures were solved by direct methods and refined by full-matrix least squares techniques by means of the SHELXT[38] and SHELXL[39] programs and Olex2 GUI.[40] The positions of hydrogen atoms were calculated corresponding to their geometrical conditions, and refined using the riding model. Atomic thermal displacement parameters for non-hydrogen atoms were refined anisotropically.

CCDC 2141717 and 2141718 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre *via* http://www.ccdc.cam.ac.uk.

To resume, it was found that the reaction of $Ta(dmpz)_5$ (dmpz is 3,5-dimethylpyrazolate) with CS_2 leads to the migration of pyrazolate groups and to the formation of the unusual complex $[Ta(=S)(dmpz)_2\{(dmpz)_3CS\}]$. This is a rare type of non-redox cleavage of a C=S bond in CS_2 with concomitant formation of a potentially interesting 'scorpionate' ligand $(dmpz)_3CS^-$.

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Online Supplementary Materials

Supplementary data associated with this article can be found in the online version at doi: 10.1016/j.mencom.2022.09.003.

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