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Verification and reinterpretation of the structure of $K_2Tc_2Cl_6$

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Abstract

The crystal structure of the title compound has been re-examined, first employing the original data and then with two new sets of data, each on a different crystal (at 15 and −53 °C). There is complete agreement between all three structures, which have Tc–Tc bond distances of 2.044(1), 2.047(1) and 2.042(2) Å. It is shown that this uniquely short Tc–Tc distance is not anomalous and can be interpreted consistently with the distances and bond orders previously found in $[Tc_2Cl_8]^{2-}$ and $[Tc_2Cl_8]^{3-}$ as that of a triple bond ($\sigma^2\pi^4\delta^2\delta^{*2}$).

Introduction

In 1986 the preparation and crystal structure of the compound $K_2[Tc_2Cl_6]$ were reported [1]. The structure was described as containing infinite chains of Tc_2Cl_8 units sharing some Cl atoms, in such a way that the formula can be more informatively written as $K_2[Tc_2Cl_4Cl_{4/2}]$. Within each $Tc_2Cl_4Cl_{4/2}$ unit the rotational conformation is staggered. The most arresting feature of the reported structure is the uniquely short Tc–Tc distance, 2.044(1) Å. When compared to the Tc–Tc distances in $[Tc_2Cl_8]^{2-}$ (2.151(1) Å) and $[Tc_2Cl_8]^{3-}$ (2.105(1), 2.117(2) Å) [2], this very close approach of the Tc atoms raised the question of whether the Tc–Tc bond order could be even higher than 4 and also whether there could possibly be any error in the reported structure.

We present here (i) confirmation of the correctness of the structure, and (ii) a discussion showing that the short distance is not inconsistent with the assignment of a Tc–Tc triple bond based on a $\sigma^2\pi^4\delta^2\delta^{*2}$ electron configuration.

Redeterminations of the crystal structure

First the original data [1] were employed at Texas A&M and the structure was re-solved and re-refined. The results were not significantly different from those previously published [1]. Following this, the compound was prepared again and crystals obtained by the previously described procedures [1].

Data were collected on two of the monoclinic, C-centered crystals with an Enraf-Nonius CAD-4 diffractometer using Mo Kα radiation. Pertinent information for crystal **1**: dimensions 0.75×0.06×0.05 m, 15 °C, $a=8.268(2)$, $b=13.943(2)$, $c=8.669(2)$ Å, $\beta=94.17(1)°$, $V=996.7(3)$ Å^3, 1252 data with $F_o^2>3\sigma(F_o^2)$. Crystal **2**: dimensions 0.3×0.04×0.03, −53 °C, $a=8.224(2)$, $b=13.924(1)$, $c=8.654(2)$ Å, $\beta=94.05°$, $V=988.5(4)$ Å^3, 1101 data with $F_o^2>3\sigma(F_o^2)$. The structures from the new data sets were solved *ab initio*, and gave solutions essentially identical to that of the previous report. The refinements included 89 parameters (as opposed to 92 reported previously) and converged to $R=0.046$, $R_w=0.089$ for crystal **1** and $R=0.062$, $R_w=0.098$ for crystal **2**.

The principal dimensions obtained in each of the new determinations are collected in Table 1 along with those from ref. 1. See also 'Supplementary material'.

Correlation of the structure with related ones

The Tc–Tc distance in this compound is considerably shorter than those in the $[Tc_2Cl_8]^{n-}$ ($n=2$, 3) ions [2], and considerably shorter than those in most quadruply-bonded Mo_2^{4+} complexes, although

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TABLE 1. Dimensions of $[Tc_2Cl_4Cl_{4/2}]^{2-}$ from three independent crystal structures[a]

Dimension	Reference 2	This work	
		15 °C	−53 °C
Tc(1)–Tc(2)	2.044(1)	2.047(1)	2.042(2)
Tc(1)–Cl(1′,2) av.	2.38(1)	2.40(1)	2.38(2)
Tc(1)–Cl(3′,5) av.	2.33(1)	2.37(3)	2.35(4)
Tc(2)–Cl(1,6) av.	2.47(3)	2.43(2)	2.46(2)
Tc(2)–Cl(3,4) av.	2.44(2)	2.42(2)	2.42(3)
Tc(2)–Cl(1,3,4,6) av.	2.46(5)	2.43(4)	2.44(5)

[a] Numbering of atoms as in ref. 2.

a few of the latter have bonds as short as 2.06 Å. In view of the fact that in a Tc_2^{4+} compound it would be natural to anticipate only a triple bond based on a $\sigma^2\pi^4\delta^2\delta^{*2}$ electron configuration, can the short distance be considered consistent with those in the $[Tc_2Cl_8]^{n-}$ species? The answer is yes, based on the following empirical argument.

We already know that from $[Tc_2Cl_8]^{2-}$ to $[Tc_2Cl_8]^{3-}$ where we have a change from Tc_2^{6+} ($\sigma^2\pi^4\delta^2$) to Tc_2^{5+} ($\sigma^2\pi^4\delta^2\delta^*$) a contraction of about 0.04 Å occurs. If we assume that the addition of another δ^* electron, to give Tc_2^{4+} ($\sigma^2\pi^4\delta^2\delta^{*2}$), causes another such contraction, and we also allow for further shrinkage of 0.02–0.04 Å for the change from an eclipsed to a staggered conformation, we expect the distance in $[Tc_2Cl_4Cl_{4/2}]^{2-}$ to be 2.03–2.05 Å, i.e. effectively the value found.

This situation further exemplifies the important point first made some years ago [3] that when changes of δ bond order are accompanied by changes in metal atom oxidation numbers, the net change in M–M distance can be as much or more influenced by the latter than the former, because δ bonding is weak. On the other hand the very strong aggregate bonding effect of the $\sigma^2\pi^4$ configuration can be altered by changes in effective charge on the metal atoms because these changes in charge slightly expand or contract the d orbitals. Thus, even though the δ bond order goes from 1 to 0 from $[Tc_2Cl_8]^{2-}$ to $[Tc_2Cl_4Cl_{4/2}]^{2-}$ the change in oxidation state, Tc_2^{6+} to Tc_2^{4+} so enhances the σ and π bonding that a substantial contraction in the Tc–Tc distance occurs. The changes from an eclipsed to a staggered rotational orientation about the Tc–Tc axis would be expected to allow an additional small reduction in bond length.

Supplementary material

Further data are available from author F.A.C. on request.

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