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4.5-Order Tc–Tc Bond in Binuclear Technetium Compounds

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Till recently the highest known bond order was 4. This value is attained in compounds having the metal–metal bond with configuration d^4–d^4, such as $Re_2Cl_8^{2-}$, $Tc_2(CH_3COO)_4Cl_2$ etc. In a recent paper [1] some evidence has been presented for 6- (or 5-) order bonds in the Mo_2 dimer in a matrix. In this paper experimental data show the possibility of 4.5-order bonds in technetium compounds, such as $Tc_2(RCOO)_4Cl$ and $[Tc_2(RCOO)_4Cl_2]^-$.

In binuclear compounds having the metal–metal bonds with d^4–d^4 configuration the quadrupole bond M–M is formed due to σ-, π- and δ-bonds. In $[Tc_2(RCOO)_4Cl_2]^-$ the additional (as compared to $Tc_2(RCOO)_4Cl_2$) electron can occupy an orbital which is either bonding or antibonding for the Tc–Tc bond. Taking into account the discussion given in [2] for $Tc_2Cl_8^{3-}$, the two most probable cases to be considered are the following:

(*1*) The electron occupies the δ^*-orbital of $b^*_{1=}$ symmetry, which is an antibonding one for the Tc–Tc bond. In this case the transition from $Tc_2(RCOO)_4Cl_2$ to $[Tc_2(RCOO)_4Cl_2]^-$ should be accompanied by an increase in Tc–Tc distance due to the Tc–Tc bond order being reduced to 3.5.

(*2*) The electron occupies an orbital of a^*_{1g} symmetry. The wave function of such an orbital can be written in the form:

$$\varphi = \alpha(s_1 + s_2) + \beta(d_{z^2(1)} + d_{z^2(2)}) + \gamma\sigma_{Cl} + \epsilon\delta(eq) + \\ + \eta(p_{z(1)} - p_{z(2)})$$

where s_i, p_i and d_i are the wave functions of the two Tc atoms, σ_{Cl} are the σ-function of $2p_z$-axial Cl atoms, σ(eq) are the σ-functions of $2p_\sigma$-equatorial O atoms. The phases of ligand functions and the signs of coefficients α, β, γ, ε and η are chosen in such a way that φ describes the bonding between Tc atoms and the weakening of Tc–Cl_{ax} and Tc–O_{eq} bonds.

There is a total of five a_{1g} levels formed on the basis of $(s_1 + s_2)$, $(p_{z(1)} - p_{z(2)})$, $(d_{z^2(1)} + d_{z^2(2)})$, σ_{Cl} and σ_O functions. Three of these levels are occupied and describe the σ-bonds Tc–Tc, Tc–O and Tc–Cl. There are also two antibonding levels a^*_{1g}, the corresponding wave functions having the different values of α, β, γ, ε and η. From general considerations one should expect the level having $|\gamma| > |\epsilon|$ to lie lower than the level having $|\epsilon| > |\gamma|$. Thus, the antibonding level of the Tc–Cl_{ax} bond is lower than the antibonding level of the Tc–O_{eq} bond. By the same token the a^*_{2u}-type antibonding levels weakening the Tc–Tc bond, due to the presence of $(s_1 - s_2)$ and $(d_{z^2(1)} - d_{z^2(2)})$ terms, should be expected to lie higher than the a^*_{1g} level*.

Table I shows the results obtained by the X-ray structure analysis for some Tc and Re compounds. If an additional electron occupies the a^*_{1g} level, then one should expect to observe a decrease in the Tc–Tc distance and an increase in the Tc–Cl_{ax} and (to a lesser extent) Tc–O_{eq} distances in compound 4 as compared to 1. The changes in bond lengths on passing from the compound $Tc_2[(CH_3)_3CCOO]_4Cl_2$ to $[Tc_2(CH_3COO)_4Cl_2]^-$ must be mainly due to the presence of an additional electron in the last compound. A change in acid must produce an insignificant effect (see the data for compounds 6 and 7 in Table I).

A comparison of data for the technetium compounds 2 and 4 shows unambiguous evidence for the a^*_{1g} level to be occuped – not the b^*_{1u} level. A decrease in Tc–Tc distance in the compound 4 as

TABLE I. Interatomic Distances (Å).

No.	Compound	M–M	M–L_{eq}	M–L_{ax}	Ref.
1	$[Tc_2Cl_8]^{3-}$	2.144(17)	2.36–2.39	–	3, 4
2	$Tc_2[(CH_3)_3CCOO]_4Cl_2$	2.192(2)	2.032(4)	2.408(4)	5
3	$Tc_2(CH_3COO)_4Cl$	2.117(1)	2.059– –2.077	2.656(1)	8
4	$[Tc_2(CH_3COO)_4Cl_2]^-$	2.1260(5)	2.069– –2.089	2.539(1)	9
5	$[Re_2Cl_8]^{2-}$	2.22–2.24	2.31–2.32	–	6
6	$Re_2[(CH_3)_3CCOO]_4Cl_2$	2.236(1)	2.025(4)	2.477(3)	5
7	$Re_2(CH_3COO)_4Cl_2$	2.2240(5)	2.041– –2.030	2.521(3)	7

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*This is confirmed by the subsequent analysis, where decreased Tc–Tc bond lengths are observed in the compound 4 (Table I) as compared to 2. It is thus not necessary to consider the cases where the highest occupied orbital is represented by the antibonding π^*-orbitals for Tc–Tc bond.

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compared to 2 is due to the following set of conditions:

(*a*) the presence of bonding interactions ($s_1 + s_2$) and ($d_{z^2(1)} + d_{z^2(2)}$);

(*b*) the weaker *trans*-influence of axial Cl ligands on Tc–Tc bond due to increased Tc–Cl distance. It should be stressed that the last change in *trans*-influence alone is insufficient to explain the observed increase in Tc–Tc distance by 0.065 Å. Indeed, in the similar Mo and Re compounds the changes in metal–metal bond lengths (as dependent on the presence or the character of axial ligand) usually do not exceed 0.03 Å [5].

At the present time the values of coefficients α, β, γ, ϵ and η are not known, since no quantum-chemical calculations have been carried out for the compound 4. In principle, it is quite possible that α and β are small. In such a case the a^*_{1g} level is on the whole an antibonding one for the Tc–Tc bond, and the bond order is 4. A small β value is highly probable because one can expect the d_{z^2} orbitals to contribute significantly to both the bonding a_{1g} and the antibonding a^*_{2u} levels of σ-bond M–M. On the other hand, an appreciable α value is quite possible. Moreover, since the technetium s- and p-functions must have the total population of 2 (for the sum along all the a_{1g} states), while the contribution of s- and p-states to occupied orbitals is small (as indicated by the available calculations for transition-metal complexes), a large α value must be reached in one a^*_{1g} orbital and a large η value in another a^*_{1g} orbital. The lower orbital is very likely to have $|\alpha| > |\eta|$, because in the free Tc atom s-states are occupied and p-states are vacant. In this case the formal electron configuration of Tc–Tc bond in the compound 4 corresponds to $d^4s^{1/2}$– $d^4s^{1/2}$ and the bond order is 4.5. It should be noted that all the obtained results are readily applicable to compound 3 which, like compound 4, has a bond order equal to either 4 or 4.5.

Finally, it should be pointed out that in $Tc_2Cl_8{}^{3-}$ both the quantum-chemical calculations and the magnetic measurements [2] show the evidence for the Tc–Tc bond order to be 3.5, *i.e.* the highest occupied level has the symmetry of b^*_{1u}. This, in principle, does not contradict our results for the compounds 3 and 4 because in these last cases the low-lying a^*_{1g} level is added which corresponds to weakening of the Tc–Tc bond. Although the available evidence [2] for the bond order value of 3.5 in $Tc_2Cl_8{}^{3-}$ is quite convincing, we consider it to be useful for purposes of discussion to quote some arguments in favour of still higher bond order in this compound. The Tc–Tc distance in $Tc_2Cl_8{}^{3-}$ is close to those values in compounds 3 and 4. Moreover, the differences of M–M and M–Cl distances in compounds 1 and 5 for M = Tc and = Re are –0.09 and 0.06 Å respectively, that is in the compound 1 the presence of an additional (as compared to the compound 5) electron can be expected to lead to either a decrease in M–M bond length, or an increase in M–Cl bond length, or both. These changes agree with the suggestion for the additional electron to occupy the a^*_{1g}-type level conducive to some strengthening of the Tc–Tc bond and weakening of the Tc–Cl bond. In this case the Tc–Tc bond order in $Tc_2Cl_8{}^{3-}$ is not less than 4.

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