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Jahn–Teller distortion of the open-shell 23-electron chalcogenide rhenium cluster cores in crystals of the series, {[Re$_6$Q$_8$]$^{3+}$(X$^-$)$_6$}$^{3-}$ (Q = S, Se; X = Cl, CN)†

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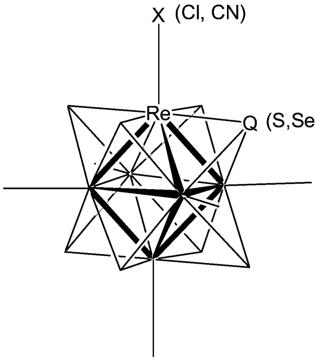
Comparison within the title [Re$_6$Q$_8$X$_6$]$^{4-}$/[Re$_6$Q$_8$X$_6$]$^{3-}$ redox series of 14 precise crystal structures of the Re$_6$ cluster cores at different low temperatures reveals that the one-electron oxidised, open-shell (23 electron) cores undergo a Jahn–Teller distortion of their parent 24 electron octahedral cores and that D_{4h} and D_{2h} forms may co-exist in the solid state.

In 1999, we reported the synthesis and structure of (Bu$_4$N-)$_3$[Re$_6$S$_8$Cl$_6$], the one-electron oxidized, open-shell member of the inorganic redox couple [Re$_6$S$_8$Cl$_6$]$^{4-}$/[Re$_6$S$_8$Cl$_6$]$^{3-\cdot}$.[1] We now report an analysis of the precise crystal structures† at different low temperatures of the set of tetrabutylammonium or tetraphenylphosphonium salts of the 23-electron cluster cores [Re$_6$Q$_8$X$_6$]$^{3-\cdot}$ (Q = S, Se; X = Cl, CN) illustrated in Scheme 1 and reveal that the 23-electron cluster cores experience diverse Jahn–Teller structural distortions.

Our primary concern has been to qualify the behavior at low temperature of the octahedral closed-shell, 24-electron core in (PPh$_4$)$_4$[Re$_6$S$_8$(CN)$_6$]·(CH$_3$CN)$_2$ **4**.[2] To that effect, a set of precise crystal structures of **4** has been determined at four different temperatures, as illustrated in Fig. 1 (black data). There is one half-cluster only in the asymmetric unit in **4** whose three independent *trans*-[Re-to-Re] distances (Table 1) are inherently different at room temperature, and indeed the cluster core seemingly departs slightly from O_h symmetry. When the temperature is lowered, the Re$_6$ core becomes increasingly more symmetrical and essentially reaches quasi-O_h symmetry down at 150 K. This tends to suggest that the lattice constraints exerted at room temperature are not quite isotropic and that the cluster core is somewhat flexible,[3] hence the 2-plus-1 pattern of *trans*-[Re-to-Re] distances in **4** at 293 K. Then, upon lowering the temperature, and although the steric constraints imposed on the cluster core site increase upon thermal contraction, they eventually become more isotropic in **4** at 150 K. One therefore concludes that the 24-electron cluster core is indeed of O_h symmetry. Therefore, the slight distortion of the octahedral core in (PPh$_4$)$_4$[Re$_6$S$_8$(CN)$_6$]·(CH$_3$CN)$_2$ at room temperature is taken as a measure of how the environment affects the flexible Re$_6$ core and we shall assume that an environment effect of similar magnitude prevails in the crystals of (PPh$_4$)$_3$[Re$_6$S$_8$(CN)$_6$].



Scheme 1 (NBu$^n{}_4{}^+$)$_3$[Re$_6$S$_8$Cl$_6$]$^{3-\cdot}$ **1** @ 293, 150, 100 K; (PPh$_4{}^+$)$_3$[Re$_6$S$_8$(CN)$_6$]$^{3-\cdot}$, **2** @ 293, 250, 200, 150 K; (PPh$_4{}^+$)$_3$[Re$_6$Se$_8$(CN)$_6$]$^{3-\cdot}$·(CH$_3$CN)(H$_2$O)$_3$ **3** @ 293, 150 K; (PPh$_4{}^+$)$_4$[Re$_6$S$_8$(CN)$_6$]$^{4-}$·(CH$_3$CN)$_2$ **4** @ 293, 250, 200, 150 K; (PPh$_4{}^+$)$_4$[Re$_6$Se$_8$(CN)$_6$]$^{4-}$·(CH$_3$CN)$_2$ **5** @ 293, 90 K.

As exemplified in Fig. 1, the 23-electron core in (PPh$_4$)$_3$[Re$_6$S$_8$(CN)$_6$] **2**, prepared from **4** by electrocrystallization in acetonitrile, as described previously[1] for **1**, is likely to be more distorted at room temperature than the former reference 24-electron core and, significantly, this distortion clearly increases when the temperature is lowered. These data are strong, convincing evidence for a Jahn–Teller distortion of the Re$_6$ cluster core in **2**. It is of interest that the two independent half-clusters in the asymmetric unit in **2** distort differently. One (red data) transforms into a D_{4h} form (Scheme 2) upon elongation of one *trans*-[Re-to-Re] distance (Table 1). The former co-exists in the lattice with its congener whose three independent *trans*-[Re-to-Re] separations (blue data) become increasingly different upon lowering the temperature (D_{2h} distortion, Scheme 2). Note that it is by lowering the temperature and achieving a situation where the steric con-

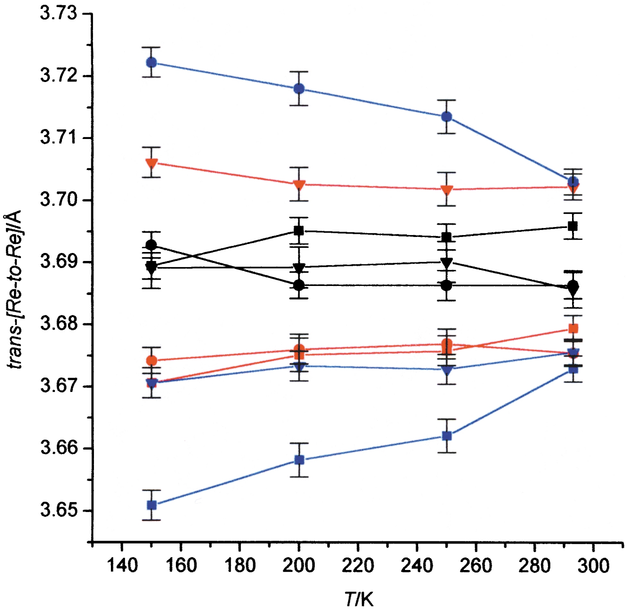


Fig. 1 Evolution upon cooling of the three independent *trans*-[Re-to-Re] (squares, circles, triangles) distances in **2** (red and blue data) and **4** (black data). Errors bars have been drawn to encompass three times the estimated standard deviations of the structure refinements.

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† Electronic supplementary information (ESI) available; crystallographic data (collected on a STOE IPDS equipped with an Oxford cryostat) and full details of solution and refinement for all 14 structures reported herein, Tables 2–6. CCDC 186991–187004. See http://www.rsc.org/suppdata/cc/b2/b205241e/ for crystallographic files in .cif or other electronic format.

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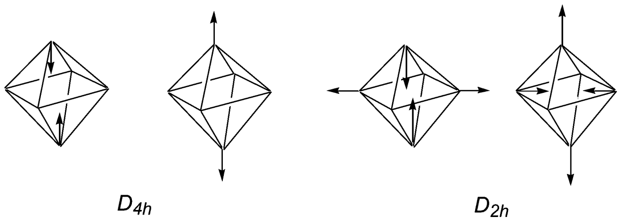
Table 1 The *trans*-[Re–Re] distances (Å) for each of the two independent cluster cores for **1**–**3**; and the single independent cluster core for **4** and **5**

	293.0(1) K		**250.0(1) K**		**200.0(1) K**		**150.0(1) K**		**100.0(1) K**		**90.0(1) K**
1	3.6772(8)	3.6675(7)					3.6977 (11)	3.6820 (11)	3.6921 (8)	3.6781 (8)	
	3.6751(7)	3.6830(11)					3.6940 (19)	3.6838(20)	3.6830 (6)	3.6510 (5)	
	3.6829(11)	3.6827(8)					3.6612 (10)	3.6855 (11)	3.6479 (5)	3.6905 (6)	
2	3.6754 (7)	3.7030 (7)	3.6769 (8)	3.7135 (9)	3.6760 (8)	3.7180 (9)	3.6742 (7)	3.7222 (8)			
	3.6794 (7)	3.6729 (7)	3.6758 (8)	3.6621 (9)	3.6751 (9)	3.6582 (9)	3.6706 (8)	3.6509 (8)			
	3.7022 (7)	3.6756 (7)	3.7018 (9)	3.6728 (8)	3.7026 (9)	3.6733 (8)	3.7061 (8)	3.6706 (8)			
3	3.7187 (5)	3.7258 (6)					3.7164 (5)	3.7350 (6)			
	3.7469 (7)	3.7188 (6)					3.7632 (6)	3.7110 (6)			
	3.7151 (6)	3.7251 (5)					3.7073 (6)	3.7292 (5)			
4	3.6863 (7)		3.6863 (8)		3.6863 (7)		3.6928 (7)				
	3.6959 (7)		3.6941 (7)		3.6951 (7)		3.6894 (7)				
	3.6857 (10)		3.6903 (11)		3.6892 (11)		3.6891 (11)				
5	3.7310 (8)										3.7327 (7)
	3.7366 (7)										3.7317 (7)
	3.7317 (10)										3.7323 (11)

The data for **1**@293 K are from reference 1.



Scheme 2 An illustration of a number of Jahn–Teller contractions and elongations of the Re_6 core yielding the D_{4h} and D_{2h} isomers.

straints on the two independent discrete, molecular clusters become both enhanced and more isotropic that the present structural distortions, expression of one single intrinsic electronic Jahn–Teller effect,[4] are expressed plainly on the *trans*-[Re-to-Re] separations discrepancies.

The observation of a D_{4h} Jahn–Teller distortion of comparable magnitude has been documented earlier by Saito *et al.* for partial occupation of the e_g orbital of the metal octahedron in the 21-electron molybdenum cluster complexes [PPN][Mo_6Q_8-$(PEt_3)_6$], (Q = S, Se).[5] These authors also pointed out that such significant, albeit weak structural manifestations of an electronic effect are revealed by virtue of the molecular character of the discrete cluster complexes, where the metal core is less constrained than in the structure-related condensed, extended solids with covalent inter-cluster bonds.

The structural Jahn–Teller activity in hexanuclear rhenium chalcogenide clusters has been qualified further by a DFT investigation reported separately.[4] The doubly degenerated HOMO of e_g symmetry of the 24-electron core splits upon one-electron oxidation into a_{1g} and b_{1g} orbitals and the ground state of the 23-electron core is calculated to be slightly more stabilized in the contracted configuration of D_{4h} symmetry than in any of the D_{2h} configurations (Scheme 2). This is indeed the situation (contracted-D_{4h}) revealed for **1** at 100 K, whose, in addition, both independent half-cluster cores experience a similar distortion. Note also, that the distortion, calculated at 0 K under vacuum, is of the order of magnitude of the observed distortions reported in Table 1.

A novel situation is encountered for **3**, prepared as described previously for the corresponding tetrabutylammonium salt,[6] in which the two half-cluster cores also undergo D_{4h} distortions (Table 1) with one elongated-D_{4h} and one slightly contracted-D_{4h} forms. Note that the single half-cluster core in the asymmetric unit of its parent 24-electron cluster in $(PPh_4)_4$-$[Re_6Se_8(CN)_6]\cdot(CH_3CN)_2$ **5**,[2] remains octahedral at 90 K (Table 1).

Further investigations will seek to determine the crystal structures of **1**–**3** in the 10–40 K temperature range in order to assess the distortion limit.

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