

provide essentially unequivocal evidence for the presence of an inductive contribution to the methyl-group aromatic-ring interaction in the toluene anion.<sup>6</sup> A subsequent paper will present a more detailed description of the HMO results and their confirmation by an ASMO-CI (Pariser-Parr) treatment.

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(6) The conclusion of J. R. Bolton, A. Carrington, and A. D. McLachlan [*Mol. Phys.*, **5**, 31 (1962)] that hyperconjugation and induction can result in equivalent energy changes appears to be incorrect; the difficulty arises from their neglect of the methyl group antibonding orbital. See, also, J. P. Colpa and E. de Boer, *ibid.*, **7**, 333 (1964).

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### A Multiple Bond between Technetium Atoms in an Octachloroditechnetate Ion<sup>1</sup>

Sir:

We wish to present a preliminary account of the results of an X-ray diffraction study of the compound  $(\text{NH}_4)_3\text{Tc}_2\text{Cl}_8 \cdot 2\text{H}_2\text{O}$  recently reported by Eakins, Humphreys, and Mellish.<sup>2</sup> The compound was prepared as directed by these authors. The unit cell has trigonal symmetry with the dimensions  $a = 13.03 \pm 0.02$  and  $c = 8.40 \pm 0.01$  Å. With three of the above formula units per cell, the calculated density is  $2.31 \text{ g. cm.}^{-3}$  ( $d_{\text{exptl}} 2.4 \text{ g. cm.}^{-3}$ ). From systematic extinctions and the three-dimensional Patterson function, the space group was found to be  $P3_121$ .

The salient feature of the structure (for which the usual reliability index now stands at 15% for 412 reflections) is the occurrence of  $\text{Tc}_2\text{Cl}_8$  groups which are essentially isostructural with the  $[\text{Re}_2\text{Cl}_8]^{2-}$  group.<sup>3,4</sup> Their virtual symmetry is  $D_{4h}$ , although, crystallographically, they possess only a single  $C_2$  axis bisecting the Tc-Tc bond. The four crystallographically independent Tc-Cl bonds have lengths of 2.34, 2.35, 2.35, and 2.36 Å., each with a standard deviation of 0.03 Å., while the Tc-Tc distance is  $2.13 \pm 0.01$  Å. Two-thirds of the ammonium ions have been located on the sixfold equipoint, lying between the  $\text{Tc}_2\text{Cl}_8$  groups, with  $N \cdots Cl$  distances of 3.04 to 3.37 Å., while the remaining ammonium ions are on a threefold equipoint.

Recent studies in this laboratory of metal atom cluster compounds,<sup>5</sup> especially those of rhenium,<sup>3</sup> have led to the preparation<sup>6</sup> and characterization<sup>4,6</sup> of the  $[\text{Re}_2\text{X}_8]^{2-}$  ions, in which there is an extremely short Re-Re bond (2.24 Å.). On the basis of the bond length and the eclipsed structure of the  $[\text{Re}_2\text{Cl}_8]^{2-}$  ion, as well as for some other reasons, it has been proposed that the Re-Re

bond is quadruple,<sup>3,7</sup> consisting of a  $\sigma$ -bond, two  $\pi$ -bonds, and a  $\delta$ -bond. It has also been suggested<sup>7</sup> that the carboxylate-bridged dimers,<sup>8</sup>  $[\text{Re}(\text{O}_2\text{CR})_2\text{X}]_2$ , have quadruple bonds; X-ray studies are in progress to test this suggestion.

The charge of  $-3$  on the  $\text{Tc}_2\text{Cl}_8$  group is somewhat surprising. However, in addition to the X-ray evidence, our own analytical data confirm the formula, and magnetic susceptibility data are consistent with the presence of one unpaired electron per  $\text{Tc}_2\text{Cl}_8$  unit.

It is of interest to compare our results for the  $\text{Tc}_2\text{Cl}_8$  group with those which have been obtained by Lawton and Mason<sup>9</sup> for Wilkinson's Mo(II) acetate.<sup>10</sup> These workers find that the compound is a centrosymmetric dimer with the acetate groups acting as bridges between the metal atoms in the same general manner as in the Cu(II) carboxylate dimers. There is a square-planar set of oxygen atoms about each Mo atom, and the Mo-Mo distance is 2.10 Å. This distance is practically the same as the Tc-Tc distance we have found in the  $\text{Tc}_2\text{Cl}_8$  ion. It appears that the formation of extremely short, presumably quadruple, bonds between  $d^4$ -ions of the second- and third-row transition elements may be quite general. Chemical and structural studies of these and related compounds are being continued.

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### The Molecular Structure of Molybdenum(II) Acetate

Sir:

We have completed an X-ray analysis of the crystal structure of molybdenum(II) acetate.<sup>1,2</sup> The crystals are triclinic, space group  $P\bar{1}$ , with  $a = 8.35$ ,  $b = 5.46$ , and  $c = 7.50$  Å.,  $\alpha = 82.9^\circ$ ,  $\beta = 105.1^\circ$ ,  $\gamma = 105.1^\circ$ ; with  $\rho_{\text{obsd}} = 2.10 \text{ g./cc.}$ ,  $Z = 1$  for  $[\text{Mo}(\text{O}_2\text{CCH}_3)_2]_2$ . The molecule is strictly centrosymmetric in the crystal, its stereochemistry being shown in Figure 1; the observed molecular dimensions are the result of a least-squares analysis of 393 reflections ( $R = 0.071$ ), average e.s.d.'s of bond lengths being 0.003 (Mo-Mo), 0.025 (Mo-O), and 0.04 Å. (C-C and C-O).

With the exception of the remarkably short metal-metal bond, the structure is similar to that of the copper acetate dimer structure,<sup>3</sup> the four bridging acetate groups establishing a slightly distorted planar configuration of each molybdenum ion. The covalent radius of the metal can be estimated from the observed mean Mo-O bond length of 2.10 Å. as 1.45 Å.,<sup>4</sup> and a metal-metal bond length of *ca.* 2.9 Å. would therefore be

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(4) The covalent radius of oxygen is given a value of 0.65 Å. as judged from the available accurately determined carbon-oxygen bond lengths.<sup>5</sup>

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