

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

Acknowledgment.—One of the authors (M. K.) wishes to thank Dr. J. M. Parks and Dr. G. K. Fraenkel for helpful discussions of the hyperconjugation problem.

(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).

D. Lazdins, M. Karplus

Department of Chemistry and IBM Watson Laboratory
Columbia University, New York, New York

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A Multiple Bond between Technetium Atoms in an Octachloroditechnetate Ion¹

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.² 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 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 Tc_2Cl_8 groups which are essentially isostructural with the $[\text{Re}_2\text{Cl}_8]^{2-}$ group.^{3,4} 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 ± 0.01 Å. Two-thirds of the ammonium ions have been located on the sixfold equipoint, lying between the Tc_2Cl_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,⁵ especially those of rhenium,³ have led to the preparation⁶ and characterization^{4,6} 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,^{3,7} consisting of a σ -bond, two π -bonds, and a δ -bond. It has also been suggested⁷ that the carboxylate-bridged dimers,⁸ $[\text{Re}(\text{O}_2\text{CR})_2\text{X}]_2$, have quadruple bonds; X-ray studies are in progress to test this suggestion.

The charge of -3 on the Tc_2Cl_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 Tc_2Cl_8 unit.

It is of interest to compare our results for the Tc_2Cl_8 group with those which have been obtained by Lawton and Mason⁹ for Wilkinson's Mo(II) acetate.¹⁰ 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 Tc_2Cl_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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(8) F. Taha and G. Wilkinson, *J. Chem. Soc.*, 5406 (1963).

(9) D. Lawton and R. Mason, *J. Am. Chem. Soc.*, **87**, 921 (1965).

(10) T. A. Stephenson, E. Bannister, and G. Wilkinson, *J. Chem. Soc.*, 2538 (1964).

F. A. Cotton, W. K. Bratton

Department of Chemistry, Massachusetts Institute of Technology
Cambridge, Massachusetts 02139

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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.^{1,2} 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,³ 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.,⁴ and a metal-metal bond length of *ca.* 2.9 Å. would therefore be

(1) E. Bannister and G. Wilkinson, *Chem. Ind. (London)*, 319 (1960).

(2) T. A. Stephenson, E. Bannister, and G. Wilkinson, *J. Chem. Soc.*, 2538 (1964).

(3) J. N. van Niekerk and F. R. L. Schoening, *Acta Cryst.*, **6**, 227 (1953).

(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.⁵

(5) "Interatomic Distances," Special Publication No. 11, The Chemical Society, London, 1958.

(1) Supported by the U. S. Atomic Energy Commission.

(2) J. D. Eakins, D. G. Humphreys, and C. E. Mellish, *J. Chem. Soc.*, 6012 (1963).

(3) F. A. Cotton, N. F. Curtis, C. B. Harris, B. F. G. Johnson, S. J. Lippard, J. T. Mague, W. R. Robinson, and J. S. Wood, *Science*, **145**, 1305 (1964).

(4) F. A. Cotton and C. B. Harris, *Inorg. Chem.*, **4**, 330 (1965).

(5) F. A. Cotton and T. E. Haas, *ibid.*, **3**, 10 (1964).

(6) F. A. Cotton, N. F. Curtis, B. F. G. Johnson, and W. R. Robinson, *ibid.*, **4**, 326 (1965).

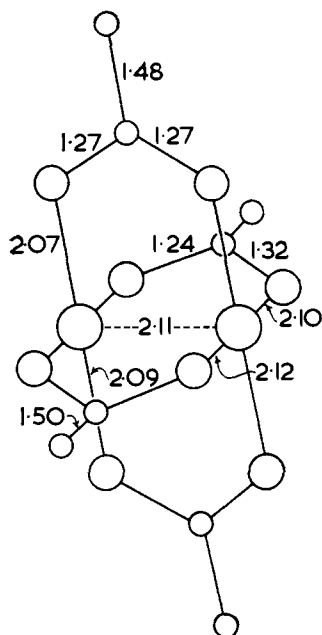


Figure 1.

expected. In copper acetate dihydrate³ and π -allyl-palladium acetate⁶ the adoption of this oxygen covalent radius taken with the mean values of the metal-oxygen bond lengths predicts metal-metal bond lengths of 2.64 Å. for Cu-Cu (observed 2.64 Å.) and 2.92 Å. for Pd-Pd (observed 2.94 Å.) so that in these binuclear systems there is no significant shortening of the metal-metal bond. The decrease of 0.8 Å. from the sum of the σ -bonded covalent radius of Mo^{2+} in the molybdenum acetate structure is similar to that reported by Cotton and Bratton⁷ for the bonding between technetium atoms in an octachloroditechnate ion and adds credence to the view that, in contrast to the d^9 -binuclear complexes mentioned above, multiple bonding between d^4 -transition metal ions of the second and third row may be of fairly general occurrence.

Details of the crystallography of molybdenum(II) acetate will be reported elsewhere when further X-ray data have been added to the refinement scheme in order to increase the accuracy of the observed ligand bond lengths.

Acknowledgment. We are grateful to the Department of Scientific and Industrial Research for support of these studies.

(6) M. R. Churchill and R. Mason, *Nature*, **204**, 777 (1964).

(7) F. A. Cotton and W. K. Bratton, *J. Am. Chem. Soc.*, **87**, 921 (1965).

D. Lawton, R. Mason

Department of Chemistry, The University Sheffield, England

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The Ionization Potential of Carbon Tetrafluoride

Sir:

The ionization and dissociation of CF_4 has been studied by both electron impact¹⁻⁵ and spectroscopic^{6,7}

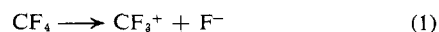
(1) L. Goldstein, *Ann. Phys. (Paris)*, [11] **9**, 723 (1938).

(2) V. H. Dibeler, R. M. Reese, and F. L. Mohler, *J. Res. Natl. Bur. Std.*, **57**, 113 (1956).

methods. The CF_4^+ ion is usually not detected in the mass spectrum of CF_4 .³⁻⁵ However, Dibeler, Reese, and Mohler² have detected a very small amount of the CF_4^+ ion (<0.01%) but reported no energetic measurements for this ion. Only one value for $I(\text{CF}_4)$, equal to 17.8 e.v.,¹ has been reported in the literature. This value is noted to be surprisingly high in view of the value of $A(\text{CF}_3^+)$ determined from CF_4 (16.0,² 15.44,³ 15.20,⁴ and 15.40 e.v.⁵). It is difficult to understand this high literature value for the ionization potential of CF_4 , since the various appearance potential measurements of CF_3^+ from CF_4 are consistent and are considerably lower than the reported $I(\text{CF}_4)$.

The work of Goldstein¹ on the ionization potential of CF_4 was done by electron impact without mass analysis. CF_3^+ is known to be the most abundant ion in the mass spectrum of CF_4 and we believe that it is likely that the measurement of $I(\text{CF}_4) = 17.8$ e.v. was actually an approximate determination of $A(\text{CF}_3^+)$ from CF_4 . This value was determined by linear extrapolation¹ and is not in extreme disagreement with our linear extrapolation value for $A(\text{CF}_3^+) = 16.4$ e.v.⁴ Cook and Ching⁸ have found using photoionization techniques that the first appearance of an ion current occurs at 15.56 ± 0.01 e.v. This also suggests that the ion current is due to CF_3^+ and not CF_4^+ .

Zobel and Duncan⁶ observed the beginning of continuous absorption in CF_4 at $120,900 \text{ cm}^{-1}$ and attributed this to the ion-pair production process



They also estimated $I(\text{CF}_4) = 14.21$ e.v. from thermochemical calculations. Later, Stokes and Duncan⁷ listed $I(\text{CF}_4) = 17.8$ e.v. However, we wish to employ the interpretation that the $120,900\text{-cm}^{-1}$ (15.0 e.v.) beginning of continuous absorption is, in fact, an upper limit to the first ionization potential of CF_4 , even as the beginning of continuous absorption in CH_2F_2 at $107,000 \text{ cm}^{-1}$ ⁹ was assigned to the second ionization potential of CH_2F_2 .⁷ In order to corroborate this value by other methods, we have made two separate thermochemical calculations. The first is based on an estimate of $\Delta H_f(\text{CF}_4^+)$, and the second uses both an estimate of $[\Delta H_f(\text{CF}_4^+) - \Delta H_f(\text{CF}_3^+)]$ and the measured value of $A(\text{CF}_3^+)$.

The heats of formation of several different ions, arranged in regular series, are presented in Table I. One notes that the heat of formation of the CX_4^+ species is 13 to 23 kcal./mole greater than $\Delta H_f(\text{CX}_3^+)$, and that this difference appears to decrease with the value of $\Delta H_f(\text{CX}_3^+)$. Thus, $\Delta H_f(\text{CF}_4^+)$ is estimated to be only some 12 ± 5 kcal./mole greater than $\Delta H_f(\text{CF}_3^+)$; therefore $\Delta H_f(\text{CF}_4^+) = 109 + 12 = (121 \pm 5)$ kcal./mole. The ionization potential of CF_4 is then calculated to be (14.7 ± 0.3) e.v. by using ΔH_f

(3) J. W. Warren and J. D. Craggs in "Mass Spectrometry," Institute of Petroleum, London, 1952, p. 36.

(4) D. L. Hobrock and R. W. Kiser, to be submitted for publication. In this paper, a mass spectrometric study of eight tetrahalomethanes, including CF_4 , is reported. We were unable to observe any CF_4^+ and therefore $I(\text{CF}_4)$ could not be determined directly.

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(6) C. R. Zobel and A. B. F. Duncan, *J. Am. Chem. Soc.*, **77**, 2611 (1955).

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(9) P. Wagner and A. B. F. Duncan, *J. Am. Chem. Soc.*, **77**, 2609 (1955).