Inorganic Compounds containing the Trifluoroacetate Group. Part V.† Mono- and Di-Adducts of Binuclear Molybdenum(II) Trifluoroacetates

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Molybdenum(II) trifluoroacetate adducts $[Mo_2(O_2CCF_3)_4X_n]^{n-}$ (n = 1, X = Cl, Br, I, O_2CCF_3, or $SnCl_3$; n = 2, X = Br or I) have been synthesised and characterised by i.r., Raman, and u.v.–visible spectroscopy. The metal–metal stretching frequencies occur in the range 382—366 cm^{-1}, that of a monoadduct being higher than that of the corresponding diadduct. The effect of addended ligands on the Mo–Mo bond in compounds of this type is discussed in the light of these and other data. The new substituted derivatives $[Et_4N]_2[Mo_2(O_2CCF_3)_3Cl_3]$ and $[Et_4N]_4[Mo_2(CN)_8]$ have been characterised.

MOLYBDENUM(II) carboxylates were first prepared by Wilkinson and his co-workers [1,2] and their dimeric nature confirmed by X-ray crystallographic studies [3,4] which identified a short metal–metal separation of *ca.* 2·1 Å. Such compounds give rise to a strong Raman effect at *ca.* 400 cm^{-1}, assigned to a vibrational mode which primarily involves stretching of the Mo–Mo bond.[4-7] These data, together with the eclipsed conformation adopted by $[Mo_2Cl_8]^{4-}$ which has a similar Mo–Mo separation (2·13 Å) [8] and ν(Mo–Mo) stretching frequency (at 349 cm^{-1}),[6] are usually taken to indicate a metal–metal quadruple bond. Complexes of the molybdenum(II) carboxylates, $[Mo_2(O_2CR)_4L_2]$, have been reported previously for L = Ph_3P,[2,6] MeOH,[6] and pyridine (py),[2,9] however, due to difficulties of purification and sensitivity,[2] only in the case of py has an analytically pure sample been isolated. The compound $[Mo_2(O_2CCF_3)_4(py)_2]$ has been shown by X-ray crystallography [9] to involve only weak co-ordination of the py ligands [Mo–N 2·548(8) Å] to give an essentially linear N–Mo–Mo–N arrangement in which the metal–metal separation [2·129(2) Å] is significantly longer than that [2·090(4) Å] in the parent trifluoroacetate.[4] Raman data support this implied weakening of the Mo–Mo bond on co-ordination of such additional ligands, the ν(Mo–Mo) stretching mode occurring at 397 and 367 cm^{-1} in $[Mo_2(O_2CCF_3)_4]$ and $[Mo_2(O_2CCF_3)_4(py)_2]$ respectively.[9]

In this paper we wish to report the preparation of new adducts of $[Mo_2(O_2CCF_3)_4]$, including $[Mo_2(O_2CCF_3)_4X_2]^{2-}$ (X = Br or I) analogous to similar derivatives known for Rh [10] and Cu,[11] and the first monoadducts of the molybdenum(II) carboxylates $[Mo_2(O_2CCF_3)_4X]^-$ (X = Cl, Br, I, O_2CCF_3, or $SnCl_3$). These salts were found to be more stable than neutral adducts of $[Mo_2(O_2CCF_3)_4]$ and their i.r., Raman, and u.v.–visible spectra have been determined. The data obtained provide evidence concerning how the Mo–Mo bond is affected by the number of addended ligands.

EXPERIMENTAL

All manipulations were carried out under anhydrous deoxygenated nitrogen using Schlenk-tube techniques. Dichloromethane was distilled from CaH_2 immediately prior to use. Acetone (May and Baker, ' Pronalys ' grade) and ethanol (James Burrough Ltd., AnalaR) were used without further purification. The complex $[Mo_2(O_2CCF_3)_4]$ was prepared by the method of Cotton and Norman [4] and $[Et_4N][SnCl_3]$ as described by Clark *et al.*[12] The salt $[Et_4N][O_2CCF_3]$ was obtained by treating $[Et_4N]Cl$ with $Ag[O_2CCF_3]$ in CH_2Cl_2; $[Et_4N]X$ (X = Cl, Br, or I) was used as supplied (B.D.H.) after drying *in vacuo* at *ca.* 110 °C where necessary and $[Et_4N]CN$ was prepared by the method of Andreades and Zahnow.[13]

I.r. spectra (2 000—200 cm^{-1}) were recorded on a Perkin-Elmer 225 grating spectrometer for Nujol mulls on CsI plates and (200—30 cm^{-1}) on a Grubb-Parsons Cube interferometer for samples contained in a Polythene matrix. Raman spectra (50—2 000 cm^{-1}) were measured on a Cary 82 laser Raman spectrometer with 6 328 Å excitation for powdered solids. Electronic spectra were measured on a Unicam SP 800 spectrophotometer and conductance data obtained with a Philips conductivity bridge. Microanalyses were carried out by the University of Manchester Microanalytical Department.

Tetraethylammonium Chlorotetrakis(trifluoroacetato)dimolybdate(II), $[Et_4N][Mo_2(O_2CCF_3)_4Cl]$.—The compound $[Mo_2(O_2CCF_3)_4]$ (0·129 g, 0·20 mmol) was dissolved in CH_2Cl_2 (120 cm^3) and a solution of $[Et_4N]Cl$ (0·033 g, 0·20 mmol) in CH_2Cl_2 (10 cm^3) added. Evaporation of solvent (*ca.* 110 cm^3) *in vacuo* at 25 °C produced a pale yellow *precipitate* which was filtered off and dried *in vacuo* at 25 °C to yield an analytically pure sample. The *salts* $[Et_4N][Mo_2(O_2CCF_3)_4X]$ (X = CF_3CO_2 or $SnCl_3$) were produced in a similar manner by reacting $[Mo_2(O_2CCF_3)_4]$ with the corresponding $[Et_4N]^+$ salt (1 : 1). However, to produce an analytically pure sample of $[Et_4N][Mo_2(O_2CCF_3)_4X]$ (X = Br or I) a 10% excess of $[Mo(O_2CCF_3)_4]$ was employed. Typical yields for these monoadduct syntheses were 50—60%.

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Bis(tetraethylammonium) Dibromotetrakis(trifluoroacetato)-dimolybdate(II), $[\mathrm{Et_4N}]_2[\mathrm{Mo_2(O_2CCF_3)_4Br_2}]$.—The compound $[\mathrm{Mo_2(O_2CCF_3)_4}]$ (0·129 g, 0·20 mmol) was dissolved in $\mathrm{CH_2Cl_2}$ (120 cm^3) and a solution of $[\mathrm{Et_4N}]\mathrm{Br}$ (0·082 g, 0·40 mmol) in $\mathrm{CH_2Cl_2}$ (15 cm^3) added. The pale yellow *precipitate* which formed immediately was filtered off and dried *in vacuo* at 25 °C to yield an analytically pure sample in *ca.* 90% yield. The *salt* $[\mathrm{Et_4N}]_2[\mathrm{Mo_2(O_2CCF_3)_4I_2}]$ was obtained in this yield for the corresponding reaction between $[\mathrm{Mo_2(O_2CCF_3)_4}]$ and $[\mathrm{Et_4N}]\mathrm{I}$ (1 : 2).

Bis(tetraethylammonium) Trichlorotris(trifluoroacetato)dimolybdate(II), $[\mathrm{Et_4N}]_2[\mathrm{Mo_2(O_2CCF_3)_3Cl_3}]$.—The compound $[\mathrm{Mo_2(O_2CCF_3)_4}]$ (0·58 g, 0·90 mmol) was dissolved in $\mathrm{CH_2Cl_2}$ (300 cm^3) and a solution of $[\mathrm{Et_4N}]\mathrm{Cl}$ (0·745 g, 4·50 mmol) in $\mathrm{CH_2Cl_2}$ (10 cm^3) added. Evaporation of solvent (*ca.* 270 cm^3) *in vacuo* at 25 °C produced a pale orange *precipitate* which was filtered off and dried *in vacuo* at 25 °C to yield an analytically pure sample. Analytically pure samples were also produced using a ten-fold excess of $[\mathrm{Et_4N}]\mathrm{Cl}$; $[\mathrm{Et_4N}]_2[\mathrm{Mo_2(O_2CCF_3)_3Cl_3}]$ was considerably less air stable than $[\mathrm{Et_4N}]_2[\mathrm{Mo_2(O_2CCF_3)_4X_2}]$ and $[\mathrm{Et_4N}][\mathrm{Mo_2(O_2CCF_3)_4X}]$ (X = Cl, Br, or I).

TABLE 1

Analytical data [a] for mono- and di-adducts of $[\mathrm{Mo_2(O_2CCF_3)_4}]$

Compound	C	H	N	Mo	X [b]	Sn
$[\mathrm{Et_4N}]_2[\mathrm{Mo_2(O_2CCF_3)_4Br_2}]$	26·6 (27·1)	3·8 (3·8)	2·3 (2·6)	17·7 (18·0)	14·5 (15·0)	
$[\mathrm{Et_4N}]_2[\mathrm{Mo_2(O_2CCF_3)_4I_2}]$	25·3 (24·9)	3·7 (3·5)	2·3 (2·4)	17·0 (16·6)	22·0 (21·9)	
$[\mathrm{Et_4N}][\mathrm{Mo_2(O_2CCF_3)_4Cl}]$	23·6 (23·7)	2·3 (2·5)	1·5 (1·7)	24·2 (23·7)	4·7 (4·4)	
$[\mathrm{Et_4N}][\mathrm{Mo_2(O_2CCF_3)_4Br}]$	22·6 (22·4)	2·3 (2·3)	1·6 (1·6)	22·1 (22·5)	9·3 (9·4)	
$[\mathrm{Et_4N}][\mathrm{Mo_2(O_2CCF_3)_4I}]$	21·6 (21·3)	2·3 (2·2)	1·3 (1·6)	21·1 (21·3)	14·4 (14·1)	
$[\mathrm{Et_4N}][\mathrm{Mo_2(O_2CCF_3)_5}]$	24·1 (24·4)	2·2 (2·2)	1·5 (1·6)	22·1 (21·6)		
$[\mathrm{Et_4N}][\mathrm{Mo_2(O_2CCF_3)_4(SnCl_3)}]$	19·4 (19·2)	1·9 (2·0)	1·3 (1·4)	19·3 (19·2)	10·3 (10·6)	11·9 (11·9)
$[\mathrm{Et_4N}]_2[\mathrm{Mo_2(O_2CCF_3)_3Cl_3}]$	29·6 (29·4)	4·4 (4·4)	3·2 (3·1)	21·7 (21·4)	11·9 (11·8)	
$[\mathrm{Et_4N}]_4[\mathrm{Mo_2(CN)_8}]$	50·3 (52·2)	8·6 (8·7)	17·7 (18·3)			

[a] Expressed as a percentage with calculated values in parentheses. [b] X = Cl, Br, or I as appropriate.

Tetrakis(tetraethylammonium) Octacyanodimolybdate(II), $[\mathrm{Et_4N}]_4[\mathrm{Mo_2(CN)_8}]$.—The compound $[\mathrm{Mo_2(O_2CCF_3)_4}]$ (0·064 g, 0·10 mmol) was dissolved in $\mathrm{CH_2Cl_2}$ (60 cm^3) and a solution of $[\mathrm{Et_4N}]\mathrm{CN}$ (0·137 g, 0·88 mmol) in $\mathrm{CH_2Cl_2}$ (15 cm^3) added. The bright blue *precipitate* which formed immediately was filtered off and dried *in vacuo* at 25 °C to yield $[\mathrm{Et_4N}]_4[\mathrm{Mo_2(CN)_8}]$. This compound was found to be extremely air sensitive.

RESULTS AND DISCUSSION

This study has clearly demonstrated that the isolation of stable adducts of $[\mathrm{Mo_2(O_2CCF_3)_4}]$ is more readily achieved if the products are salts rather than neutral molecules.[2,6,9] This is presumably due in large measure to the lattice energy of these salts. The analytical data obtained for the new compounds isolated in this work are given in Table 1. The mono- and di-adducts of $[\mathrm{Mo_2(O_2CCF_3)_4}]$ are pale yellow crystalline solids which do not melt but decompose at temperatures between 165 and 210 °C. The molar conductances recorded for these compounds are consistent with the formulation of the monoadducts (147—162 S cm^2 mol^{-1}) as 1 : 1 and the diadducts (295—353 S cm^2 mol^{-1}) as 2 : 1 electrolytes.[14]

Vibrational spectra were recorded for the mono- and di-adducts between 2 000 and 50 cm^{-1}. The vast majority of the bands observed closely resemble the corresponding features [4,15] for $[\mathrm{Mo_2(O_2CCF_3)_4}]$. A typical set of vibrational data is presented in Table 2 for $[\mathrm{Et_4N}]_2[\mathrm{Mo_2(O_2CCF_3)_4I_2}]$. The vibrational spectra thus indicate that the $[\mathrm{Mo_2(O_2CCF_3)_4}]$ unit is retained in these mono- and di-adducts. In particular the position of the asymmetric carboxylato-stretching frequency (*ca.* 1 611 cm^{-1}) is not consistent [15] with a unidentate trifluoroacetato-group in this system {see below, $[\mathrm{Et_4N}][\mathrm{Mo_2(O_2CCF_3)_5}]$}. Furthermore, for the halide adducts no strong vibrations additional to those identified for $[\mathrm{Mo_2(O_2CCF_3)_4}]$ were observed at *ca.* 300 cm^{-1}, whereas $[\mathrm{Et_4N}]_2[\mathrm{Mo_2(O_2CCF_3)_3Cl_3}]$ exhibited bands at 346, 309, 282 (i.r.), and 289 (Raman) cm^{-1} characteristic [16] of Mo–Cl stretching modes. The retention of the $[\mathrm{Mo_2(O_2CCF_3)_4}]$ unit in the mono- and di-adducts salts is also consistent with the electronic spectral data recorded for these compounds. The mono- and di-adducts of $[\mathrm{Mo_2(O_2CCF_3)_4}]$ have spectra which closely resemble that of the parent compound ($\lambda_{\mathrm{max.}}$ 430, 340, and 310—300 nm with ε 130—170, 4 600—7 300, and 5 200—9 000 l mol^{-1} cm^{-1}, respectively), whereas that of $[\mathrm{Et_4N}]_2[\mathrm{Mo_2(O_2CCF_3)_3Cl_3}]$ is significantly different ($\lambda_{\mathrm{max.}}$ 477, 340, and 285 nm, with ε 280, 440, and 6 700 l mol^{-1} cm^{-1}, respectively).

TABLE 2

Vibrational spectroscopic data (2 000—50 cm^{-1}) for $[\mathrm{Et_4N}]_2[\mathrm{Mo_2(O_2CCF_3)_4I_2}]$

I.r.	1 611s, 1 490w, 1 395m, 1 300w, 1 233m, 1 195s, 1 171m, 1 147s, 1 055vw, 999w, 854m, 787vw (sh), 782w (sh), 777w, 728s, 678w, 624vw, 526w, 511w, 491w, 378w, 350vw, 327w, 297vw, 240w, 229w, 144m, 94s, 58s
Raman	1 553w, 1 494w, 1 448vs, 1 219w, 1 120w, 1 073w 1 004w, 942w, 868w, 741m, 675m, 496s, 419m, 368s, 185s, 142m, 66vs

vs = Very strong, s = strong, m = medium, w = weak, vw = very weak, and sh = shoulder.

Table 3 lists selected vibrational spectroscopic data for these salt adducts. These data appear to provide evidence concerning the structure of these salts and the

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nature of their Mo–X bond(s). The anions $[Mo_2(O_2CCF_3)_4X_2]^{2-}$ (X = Br or I) appear to have the structure (I), the halide ions adding to both axial positions of $[Mo_2(O_2CCF_3)_4]$ in a manner analogous to that characterised for $[Mo_2(O_2CCF_3)_4(py)_2]$. This structure is suggested in the light of the above comments and also because these diadducts only exhibit one asymmetric CO_2 stretching frequency and do not have the ν(Mo–Mo) stretch i.r. active, consistent with a $Mo_2(O_2C)_4X_2$ moiety possessing D_{4h} symmetry (see below). There appear to be three possible structures for the $[Et_4N][Mo_2(O_2CCF_3)_4X]$ (X = Cl, Br, I, CF_3CO_2, or $SnCl_3$) salts: (*i*) that comprising the discrete anions illustrated in (II); (*ii*) a structure similar to that identified[17] for $[Ru_2(O_2CC_3H_7)_4Cl]$ in which the Cl groups bridge adjacent $Ru_2(O_2CC_3H_7)_4$ centres; and (*iii*) one related to that of $[Rh_2(O_2CH)_4]\cdot OH_2$ which consists[10] of equal numbers of $[Rh_2(O_2CH)_4]$ and $[Rh_2(O_2CH)_4(OH_2)_2]$ molecules. This last arrangement is discounted since the monoadducts exhibit only one ν(Mo–Mo) stretching frequency and, more importantly, do not exhibit a Raman effect at *ca.* 397 cm^{-1} characteristic of $[Mo_2(O_2CCF_3)_4]$. A structure containing the discrete anions of (II) is preferred over a polymeric arrangement with bridging X groups for two reasons. First, because the properties (*e.g.* solubility and vibrational spectra) of the adduct formed by the non-bridging $[SnCl_3]^-$ ligand are very similar in essentials to those of corresponding adducts containing the potentially bridging Cl^-, Br^-, I^-, or $CF_3CO_2^-$ ligands. Secondly, the appearance of two strong asymmetric CO_2^- stretching frequencies in the i.r. is consistent with a lowering of the symmetry of the $Mo_2(O_2C)_4$ moiety from the essentially D_{4h} found[4] for $[Mo_2(O_2CCF_3)_4]$ which would be retained in a symmetrically bridged adduct structure. For D_{4h} symmetry only one (A_{2u}) asymmetric CO_2-stretching mode should be i.r. active, as found for $[Mo_2(O_2CCF_3)_4]$ and $[Et_4N]_2[Mo_2(O_2CCF_3)_4X_2]$ (X = Br or I), whereas for C_{4v} symmetry two (A_1, E) such modes should be i.r. active. For all the monoadducts reported here {excepting $[Et_4N][Mo_2(O_2CCF_3)_5]$} two strong bands attributable to asymmetric CO_2-stretching modes of the $[Mo_2(O_2CCF_3)_4]$ unit were observed between 1 600 and 1 625 cm^{-1}. Similar group theoretical arguments extend to the symmetric CO_2-stretching modes. These, however, are only weakly i.r. active and may be confused with absorptions due to $[Et_4N]^+$ near 1 400 cm^{-1}. The additional frequencies listed in Table 3 for $[Et_4N][Mo_2(O_2CCF_3)_5]$ (with the possible exception of the strong Raman effect at 968 cm^{-1}) may be attributed[15] to internal vibrations of the addended trifluoroacetato-group co-ordinated in a unidentate manner.

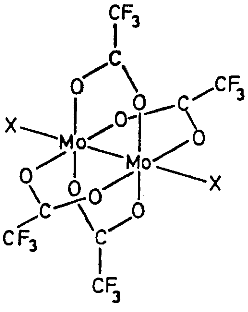
TABLE 3

Selected vibrational spectroscopic data (cm^{-1}) for mono- and di-adducts of $[Mo_2(O_2CCF_3)_4]$

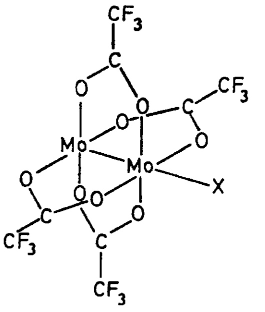
Compound	CO_2 asym. str.[a]	Mo–Mo str.[b]	Additional bands[c]
$[Et_4N][Mo_2(O_2CCF_3)_4Cl]$	1 622s, 1 609s	373s	116w[b]
$[Et_4N][Mo_2(O_2CCF_3)_4Br]$	1 622s, 1 610s	377s	85s[b]
$[Et_4N][Mo_2(O_2CCF_3)_4I]$	1 612s (sh), 1 606s	377s	71vs[b]
$[Et_4N][Mo_2(O_2CCF_3)_5]$	1 611s	379s	1 655s, 838w, 794w, 723w, 667vw,[a] 1 116vs, 968s, 676vs[b]
$[Et_4N][Mo_2(O_2CCF_3)_4(SnCl_3)]$	1 625w, 1 608s (sh), 1 600s	382s	293m, 247w, 117w[b]
$[Et_4N]_2[Mo_2(O_2CCF_3)_4Br_2]$	1 613s	366s	151w, 103s, 84s, 64s,[a] 82s[b]
$[Et_4N]_2[Mo_2(O_2CCF_3)_4I_2]$	1 611s	368s	144m, 94s, 58s,[a] 66vs[b]
$[Et_4N]_2[Mo_2(O_2CCF_3)_3Cl_3]$	1 619s (sh), 1 615s	385s and/or 362s	346m, 309m, 282w,[a] 324w, 289m, 249m[b]

s = Strong, sh = shoulder, m = medium, w = weak, vw = very weak, str. = stretch, and asym. = asymmetric.

[a] I.r. data. [b] Raman data. [c] Bands not attributable to modes of either $[Mo_2(O_2CCF_3)_4]$ or $[Et_4N]^+$.



(I) X = Br or I



(II) X = Cl, Br, I, CF_3CO_2, or $SnCl_3$

The lowest-frequency Raman effect observed for the halide adducts varies as 116w, 85s, and 71vs cm^{-1} for $[Et_4N][Mo_2(O_2CCF_3)_4X]$ (X = Cl, Br, or I) and as 82s and 66vs cm^{-1} for $[Et_4N]_2[Mo_2(O_2CCF_3)_4X_2]$ (X = Br or I), respectively. These low-frequency vibrations are considered to involve ' rattling ' of the halide ions in an essentially electrostatic potential well, with little covalent interaction between molybdenum and the halide ion. Thus the frequency of the halide vibrations varies as *ca.* $(1/m_X)^{1/2}$ (where m_X is the atomic weight of the halide) and the intensity of Raman scattering correlates roughly with the atomic number of the halide. These points, together with the relative insensitivity of ν(Mo–Mo) to the nature of the addended halide ion, suggest that there is no real kinematic coupling between halide ' rattling ' and metal–metal stretching modes. The analysis presented in the Appendix reinforces this view. The unimportance of covalent bonding between the molybdenum and addended ligands in these adducts is of course consistent with the long Mo–N bond lengths found[9] for $[Mo(O_2CCF_3)_4(py)_2]$,

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[17] M. J. Bennett, K. G. Caulton, and F. A. Cotton, *Inorg. Chem.*, 1969, **8**, 1.

and also with the results of the molecular-orbital calculations of Norman and Kolari [18] which suggest that the molybdenum atoms in these systems have no orbitals available to accommodate the electron pair(s) donated by the axial ligand(s). Presumably, therefore, the attraction between the metal atom and the axial ligand is due mainly to an electrostatic Mo$^+$L$^-$ interaction. Also the lengthening and apparent weakening of the Mo–Mo bond which results on adduct formation by $[Mo_2(O_2CCF_3)_4]$ may be attributed to the effect of placing one or two negative charges on the axial positions.

The compound $[Mo_2(O_2CCF_3)_4(PPh_3)_2]$, previously reported by Ketteringham and Oldham,[6] was also studied since these authors reported no analytical data and it seemed possible, in view of their value for the ν(Mo–Mo) stretching frequency of 377 cm^{-1}, that the compound might be the monoadduct. This may be the case; however, all our preparations of this compound, even with $[Mo_2(O_2CCF_3)_4]$: Ph_3P ratios of 1 : 1, afforded a diadduct (Found: C, 44·6; H, 2·9. Calc.: C, 45·2; H, 2·6%) which exhibited a Raman effect due to ν(Mo–Mo) at 367 cm^{-1}.

Attempted preparations of $[Et_4N]_2[Mo_2(O_2CCF_3)_4Cl_2]$ were always unsuccessful. Either the monochloro-adduct was obtained or at $[Et_4N]Cl$: $[Mo_2(O_2CCF_3)_4]$ ratios of *ca.* 5 : 1 substitution of trifluoroacetate by chloride occurred to produce $[Et_4N]_2[Mo_2(O_2CCF_3)_3Cl_3]$. The vibrational data presented in Table 3 for this latter compound, in particular the large number of bands between 346 and 282 cm^{-1} which may be attributed [16] to Mo–Cl stretching modes and the possibility of two Mo–Mo stretching modes, are taken to indicate that this compound consists of more than one Mo–Mo unit. The information presently available, however, does not allow a definite assignment of the structure of this compound to be made. It is of interest to note that the substitution of trifluoroacetate by chloride leads to a marked change in the electronic spectrum. We therefore suggest that when $[Mo_2(O_2CCF_3)_4]$ is dissolved in pyridine [9] some substitution occurs in solution {although $[Mo_2(O_2CCF_3)_4(py)_2]$ is obtained from this solution} as not only is the Mo–Mo stretch for the solution species remarkably different from that of $[Mo_2(O_2CCF_3)_4(py)_2]$ but also the electronic spectrum is considerably different from that of $[Mo_2(O_2CCF_3)_4]$. Complete replacement of trifluoroacetate appears to be readily achieved by treating $[Mo_2(O_2CCF_3)_4]$ with $[Et_4N]CN$. The bright blue compound $[Et_4N]_4[Mo_2(CN)_8]$ was found to be rather unstable and complete characterisation has not yet been achieved.

APPENDIX

One way to assess the molybdenum–halogen bond strength and the effect of addended halide(s) on the Mo–Mo bond of $[Mo_2(O_2CCF_3)_4]$ is to estimate the force constants for these bonds. These were obtained for $[Mo_2(O_2CCF_3)_4X_2]^{2-}$ (X = Br or I) and $[Mo_2(O_2CCF_3)_4X]^-$ (X = Cl, Br, or I) using the treatment described by Herzberg [19] for C_2H_2 and HCN, respectively. Effects due to the carboxylato-groups were ignored and therefore the results of such calculations (Table 4) have relative rather than absolute significance. For the diadducts, as a test of the validity of this approach, the frequency of Σ_u^+, the asymmetric halide-stretching mode of $[Mo_2(O_2CCF_3)_4X_2]^{2-}$ (X = Br or I), may be computed knowing f_{Mo-Mo} and f_{M-X}. This frequency is calculated for the dibromo-adduct as 114 cm^{-1} and for the di-iodo-adduct as 99 cm^{-1}; these values may be correlated with the strong i.r. bands observed at 103 and 94 cm^{-1}, respectively, for these ions.

TABLE 4

Force constants calculated [a] for halide adducts of $[Mo_2(O_2CCF_3)_4]$

Compound	$\bar{\nu}$(Mo–Mo)/ cm^{-1}	$\bar{\nu}$(Mo–X)/ cm^{-1}	f_{Mo-Mo}/ N m^{-1}	f_{Mo-X}/ N m^{-1}
$[Mo_2(O_2CCF_3)_4]$	397		446 [b]	
$[Mo_2(O_2CCF_3)_4Cl]^-$	373	116	387	24
$[Mo_2(O_2CCF_3)_4Br]^-$	377	85	396	24
$[Mo_2(O_2CCF_3)_4I]^-$	377	71	395	23
$[Mo_2(O_2CCF_3)_4Br_2]^{2-}$	366	82 [c]	362	33
$[Mo_2(O_2CCF_3)_4I_2]^{2-}$	368	66 [c]	366	34

[a] Using the methods described by Herzberg.[19] [b] Calculated using the simple harmonic approximation. [c] Raman active; symmetric halide-stretching frequency, Σ_g^+.

The results of these force-constant calculations appear to reinforce the arguments presented earlier based on consideration of vibrational frequencies alone. The invariance of the value of f_{Mo-X} with the nature of X for the mono- and di-adducts suggests that no real covalency is involved over the Mo–X distance(s). The higher values of f_{Mo-X} for the diadducts may be genuine or result from approximations implicit in the calculations.

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