Inorganic Compounds containing the Trifluoroacetate Group. Part VI.[1] Reactions of Molybdenum(II) Trifluoroacetate with 2,2′-Bipyridyl

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The reaction between $[Mo_2(O_2CCF_3)_4]$ and 2,2′-bipyridyl (1 : 2) has been investigated in several solvents, and four different adducts, two 1 : 1 and two 1 : 2 compounds, have been isolated and characterised. The reaction between $[Mo_2(O_2CCF_3)_4]$, 2,2′-bipyridyl, and $[OEt_3][BF_4]$ (1 : 2 : 2) has been shown to produce $[Mo_2(O_2CCF_3)_2(bipy)_2][BF_4]_2$. Structures have been assigned to these compounds on the basis of spectroscopic data and the nature of the solution species, from which the various adducts originate, is discussed.

DESPITE the variety of complexes known[2] for the dimolybdenum(II) and related dimeric halogeno-complexes, the co-ordination chemistry of the molybdenum(II) carboxylates has been almost exclusively confined to the formation of a variety of mono-[1] and bis-[1,3-5] adducts with unidentate ligands weakly bridging at the axial positions of the dimeric unit. This report describes the reactions of molybdenum(II) trifluoroacetate with 2,2′-bipyridyl under various conditions and the results obtained illustrate the potential versatility in the co-ordination chemistry available for the dimeric molybdenum(II) carboxylates.

EXPERIMENTAL

All manipulations were carried out under anhydrous, deoxygenated nitrogen using Schlenk-tube techniques. Solvents (B.D.H.) were purified in the following manner immediately prior to use. Dichloromethane and tetrahydrofuran were distilled from CaH_2, diethyl ether distilled from $Li[AlH_4]$ and carbon tetrachloride, methyl cyanide, and benzene were purged with nitrogen. Acetone (May and Baker, Pronalys grade) and ethanol (James Burrough Ltd., AnalaR quality) were used without further purification. 2,2′-Bipyridyl (Hopkins and Williams) was used as supplied, as were all other chemicals. $[OEt_3][BF_4]$,[6]

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[4] A. P. Ketteringham and C. Oldham, *J.C.S. Dalton*, 1973, 1067.

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[6] H. Meerwein, *Org. Synth.*, 1966, **46**, 113.

$[Mo_2(O_2CCF_3)_4]$,[7] and $[Mo_2(bipy)_2Cl_4]$ [8] were prepared as described previously.

TABLE 1

Analytical data [a] (%) obtained for molybdenum(II) trifluoroacetate–2,2′-bipyridyl complexes; calculated figures in parentheses

Compound	C	H	N	Mo
(I)	28.7	1.3	3.8	24.2
	(27.0)	(1.0)	(3.5)	(24.0)
(II)	28.9	1.5	3.8	23.6
	(27.0)	(1.0)	(3.5)	(24.0)
(III)	35.3	1.9	5.8	20.5
	(35.1)	(1.7)	(5.9)	(20.1)
(IV)	35.1	1.7	5.7	19.9
	(35.1)	(1.7)	(5.9)	(20.1)
(V)	34.6	2.9	5.6	19.7
	(34.4)	(2.7)	(5.7)	(19.6)

TABLE 2

X-Ray powder diffraction data [a] (Å) recorded for mono- and bis-2,2′-bipyridyl adducts of $[Mo_2(O_2CCF_3)_4]$

$[Mo_2(O_2CCF_3)_4(C_{10}H_8N_2)]$		$[Mo_2(O_2CCF_3)_4(C_{10}H_8N_2)_2]$	
(I)	(II)	(III)	(V)
9.2vs	9.2vs	9.8m	9.1vs
7.6s	7.3m	8.8vs	7.9m
6.7s	7.0m	7.1s	7.0m
5.6m	6.5s	6.5s	6.5m
5.1w	5.5m	5.9m	6.0w
4.8s	5.0vw	5.5w	5.4m
4.5s	4.5m	5.1w	5.1m
3.8s	4.1vs	4.8m	4.5s
3.6vw	3.9vw	4.5w	4.3s
3.0vw	3.8m	4.3vs	4.1s
2.7w	3.6w	4.0w	3.9s
2.5w	3.4m	3.8s	3.7s
	3.2w	3.6vw	3.5w
	3.0w	3.5m	3.4w
	2.9w	3.4m	2.9w
	2.7vw	3.1vw	
	2.6w	2.8s	
		2.5m	

[a] vs = very strong, s = strong, m = medium, w = weak, vw = very weak.

I.r. spectra were recorded on a Perkin-Elmer 257 grating spectrophotometer between NaCl plates. Electronic spectral data were obtained using a Unicam SP 800 spectrophotometer, *X*-ray powder diffraction data with a Debye-Scherrer Camera, and conductance data with a Philips conductivity bridge. Microanalyses and molecular-weight determinations were carried out by the staff of the University of Manchester Microanalytical Department.

2,2′-Bipyridyltetrakis(trifluoroacetato)dimolybdenum(II), $[Mo_2(O_2CCF_3)_4(C_{10}H_8N_2)]$ (I).—$[Mo_2(O_2CCF_3)_4]$ (0.129 g, 0.20 mmol) was dissolved in CH_2Cl_2 (50 cm^3) and a solution of 2,2′-bipyridyl (0.063 g, 0.40 mmol) in CH_2Cl_2 (5 cm^3) was added. A red solution resulted from which a microcrystalline pink solid precipitated. This suspension was stirred at 25 °C for *ca.* 10 min before the solid was filtered off and dried *in vacuo* at 25 °C to give a pink–copper coloured material.

2,2′-Bipyridyltetrakis(trifluoroacetato)dimolybdenum(II) $[Mo_2(O_2CCF_3)_4(C_{10}H_8N_2)]$ (II).—2,2′-Bipyridyl (0.063 g, 0.40 mmol) was dissolved in CCl_4 (5 cm^3) and added to a suspension of $[Mo_2(O_2CCF_3)_4]$ (0.129 g, 0.20 mmol) in CCl_4 (70 cm^3). A purple precipitate was formed immediately and, after stirring this suspension at 25 °C for 1 h, the solid was filtered off and dried *in vacuo* at 25 °C.

Bis(2,2′-bipyridyl)tetrakis(trifluoroacetato)dimolybdenum(II) $[Mo_2(O_2CCF_3)_4(C_{10}H_8N_2)_2]$ (III).—$[Mo_2(O_2CCF_3)_4]$ (0.129 g, 0.20 mmol) was dissolved in acetone (20 cm^3) and a solution of 2,2′-bipyridyl (0.063 g, 0.40 mmol) in acetone (5 cm^3) was added to it. A red-brown precipitate was obtained immediately and the resultant suspension was stirred at 25 °C for *ca.* 10 min before the solid was filtered off and dried *in vacuo* at 25 °C.

Bis(2,2′-bipyridyl)tetrakis(trifluoroacetato)dimolybdenum(II) $[Mo_2(O_2CCF_3)_4(C_{10}H_8N_2)_2]$ (IV).—$[Mo_2(O_2CCF_3)_4]$ (0.129 g, 0.20 mmol) was dissolved in ether (10 cm^3) and a solution of 2,2′-bipyridyl (0.063 g, 0.40 mmol) in ether (5 cm^3) was added to it. The purple precipitate which formed immediately was filtered off and dried *in vacuo* at 25 °C.

Bis(2,2′-bipyridyl)bis(trifluoroacetato)dimolybdenum(II) *Bis(tetrafluoroborate)—Diethyl Ether* $[Mo_2(O_2CCF_3)_2(C_{10}H_8N_2)_2][BF_4]_2{\cdot}OEt_2$ (V).—To $[Mo_2(O_2CCF_3)_4]$ (0.129 g, 0.20 mmol) and $[OEt_3][BF_4]$ (0.076 g, 0.40 mmol) dissolved in CH_2Cl_2 (60 cm^3) was added a solution of 2,2′-bipyridyl (0.063 g, 0.40 mmol) in CH_2Cl_2 (5 cm^3). The pink precipitate which formed immediately was filtered off and dried *in vacuo* at 25 °C.

Typical yields for all of these reactions were >90% based on $[Mo_2(O_2CCF_3)_4]$; Table 1 summarises the analytical data obtained for the compounds (I)—(V). The Scheme includes the above information concerning the preparation of the compounds (I)—(V) and also indicates alternative routes to these compounds.

The mass spectra of compounds (I)—(V) were recorded at *ca.* 150 °C and yielded only fragments of $[Mo_2(O_2CCF_3)_4]$ and 2,2′-bipyridyl.

TABLE 3

Electronic spectra of molybdenum(II) trifluoroacetate–2,2′-bipyridyl complexes

Compound	Phase	$\lambda_{max.}$/nm ($\varepsilon \times 10^{-3}$, l mol^{-1} cm)						
(I)	Nujol mull		500	350	315		[a]	240	
$[Mo_2(O_2CCF_3)_4]$ + $C_{10}H_8N_2$ (1 : 2)	CH_2Cl_2 [b]		520 (0.4)	350 (4)	320 (7)	307 (11)	285 (27)	245 (20)	238 (21)
(II)	Nujol mull	560	506	360	315				
(III)	Nujol mull		500	350	315			240	
$[Mo_2(O_2CCF_3)_4]$ + $C_{10}H_8N_2$ (1 : 2)	MeCN [b]		518 (0.4)	350 (4)	317 (20)	307 (24)			238 (25)
$[Mo_2(O_2CCF_3)_4]$ + $C_{10}H_8N_2$ (1 : 2)	EtOH [b]		514 (0.2)	350 (5)	320 (18)	309 (20)	282 (20)	243 (21)	237 (21)
(IV)	Nujol mull	540		350	315		[a]	250	
(V)	Nujol mull		501	350	315				
(V)	EtOH [c]		525 (0.7)	350 (6)	320 (25)	307 (31)		243 (34)	

[a] Weak shoulder observed at 275 nm. [b] Concentration 2 × 10^{-4} mol l^{-1}. [c] Concentration 5 × 10^{-4} mol l^{-1}.

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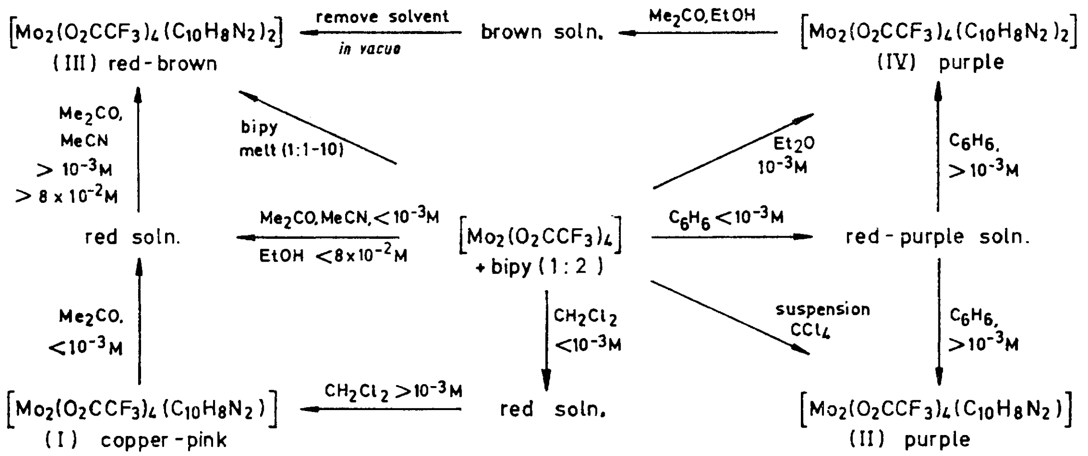
[8] A. R. Bowen and H. Taube, *Inorg. Chem.*, 1974, **13**, 2245.

RESULTS AND DISCUSSION

The reaction between $[Mo_2(O_2CCF_3)_4]$ and 2,2′-bipyridyl (1 : 2) (see Scheme) is a versatile one. The data presented in Tables 1—3 and Figure 1 establish that either one of two 1 : 1 adducts [(I) or (II)] or one of two 1 : 2 adducts [(III) or (IV)] may be obtained as the solid product from various solutions, the actual compound obtained apparently being determined by the nature of the solvent. Furthermore, spectral and other data are consistent with adducts other than (I)-(IV) being present in solution species in these various solvents.



SCHEME Reactions of $[Mo_2(O_2CCF_3)_4]$ with 2,2′-bipyridyl

The i.r. spectra of co-ordinated 2,2′-bipyridyl groups have been described.[9] Typical absorptions include one at *ca.* 1 605 cm^{-1}, with a low-energy shoulder, and bands between 770 and 720 cm^{-1}. For comparison with the i.r. spectra recorded here, we have also prepared [8] and recorded the i.r. spectrum of $[Mo_2(bipy)_2Cl_4]$ and the relevant spectral regions are reproduced in Figure 1 h. The i.r. spectra of all the compounds reported in this study appear to contain such features (see Figure 1 a—e) and therefore we conclude that the compounds (I)—(V) all contain co-ordinated 2,2′-bipyridyl groups. The electronic spectral data (Table 3) recorded for these compounds are also consistent [9] with the presence of co-ordinated 2,2′-bipyridyl groups which give rise to the absorptions at *ca.* 240 and 308 nm. The only mode of co-ordination for 2,2′-bipyridyl which has been definitely established [9] is that in which this ligand functions as a bidentate chelate to a single metal atom. Therefore, it is suggested that this mode of co-ordination is obtained exclusively in the compounds (I)—(V). One mode of co-ordination of 2,2′-bipyridyl to a dimolybdenum(II) centre which is, in principle, possible is that in which this ligand spans the Mo–Mo bond. However, we rule this out on two counts. First, molecular-model studies suggest that this is not possible without considerable strains within the ligand. Secondly, preliminary studies with 1,10-phenanthroline, a ligand that certainly cannot span the Mo–Mo distance, appear to give compounds analogous to (I)—(V) with $[Mo_2(O_2CCF_3)_4]$.

Figures 1f, 1g, and 1a—e reproduce the i.r. spectra of $[Mo_2(O_2CCF_3)_4]$, $[NEt_4][CF_3CO_2]$, and the compounds (I)—(V), respectively, in the regions in which the (OCO) asymmetric and (C–C) stretching, and (OCO) and (CF_3) deformation modes are anticipated.[10] These data clearly indicate that the atomic arrangement of the $\{Mo_2(O_2CCF_3)_4\}$ moiety established [7] for the parent compound is not obtained in the compounds (I)—(IV). This inference is also supported by the electronic spectral data recorded for these compounds (Table 3), the lowest-energy absorption of which varies between *ca.* 560 and 500 nm and is assigned [11,12] to the $\delta \rightarrow \delta^*$ transition of each Mo$\equiv$Mo unit. Unfortunately, none of these compounds gave satisfactory Raman data and thus no vibrational frequencies for their ν(Mo–Mo) stretching modes are available.

The versatility of the trifluoroacetate group as a ligand [10] and the co-ordination sites available within a dimolybdenum framework result in a large number of possible structures for the adducts $[Mo_2(bipy)_n(O_2CCF_3)_4]$ ($n = 1$ or 2). A definitive structural assignment for (I)—(V) is thus not possible in the absence of *X*-ray crystallographic data. However, the vibrational spectroscopic data presented in Figure 1 do allow certain predictions to be made in this respect. The use of vibrational spectroscopy as a probe for the mode of bonding of trifluoroacetate groups involves some difficulties.[10] Thus it is not possible to describe precise frequencies for each type of trifluoroacetate group, even though the vibrational frequencies of these groups are sensitive to the nature of their bonding to a metal centre, since these frequencies will also be influenced by other effects, in particular the nature of the metal centre. However, since each of the compounds (I)—(V) almost

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[11] R. J. H. Clark and M. L. Franks, *J.C.S. Chem. Comm.*, 1974, 316.

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certainly contains trifluoroacetate groups bonded to a dimolybdenum(II) centre, the discrimination between the various types of trifluoroacetate group by i.r. data should be relatively simple. In the course of an earlier study,[1] i.r. data were obtained for the species $[Mo_2(O_2CCF_3)_4X_n]^{n-}$ (where $n = 0$; $n = 1$, X = Cl, Br, I, CF_3CO_2, or $SnCl_3$; $n = 2$, X = Br or I), all of which apparently contain four trifluoroacetato groups-bridging across the dimolybdenum(II) centre. The (OCO) asymmetric and (C–C) stretching and (OCO) and (CF_3) deformation modes of these bridging trifluoroacetato-groups occur in the ranges 1 625—1 589, 860—855, 780—775, and 735—728 cm^{-1}, respectively. In contrast the corresponding i.r. frequencies for ionic trifluoroacetate, for example $[NEt_4][CF_3CO_2]$, occur at 1 692, 823, 803, and 719 cm, respectively. It is noted that the highest (OCO) asymmetric stretching frequencies are expected to be found for unidentate trifluoroacetato-groups and that this frequency for bidentate trifluoroacetato-groups is anticipated to be close to that observed for ionic and bridging trifluoroacetato-groups involving similar metal centres.[10]

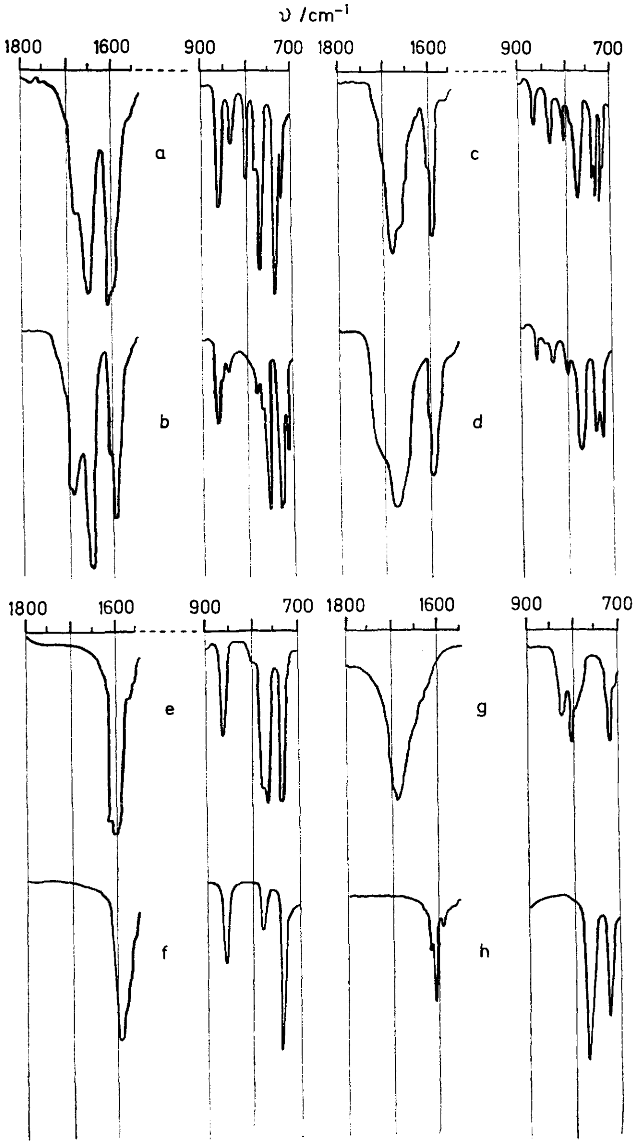

FIGURE 1 Selected i.r. data for $[Mo_2(O_2CCF_3)_4]$–2,2′-bipyridyl and related compounds: a = (I), b = (II), c = (III), d = (IV), e = (V), f = $[Mo_2(O_2CCF_3)_4]$, g = $[NEt_4][CF_3CO_2]$, h = $[Mo_2(bipy)_2Cl_4]$

These vibrational spectroscopic considerations allow some suggestions concerning the number of different types of trifluoroacetate groups and their nature, present in the compounds (I)—(V). The absorptions at *ca.* 1 604, 863, 774, and 735 cm^{-1}, together with the absence of other bands in these regions which might be ascribed to trifluoroacetate groups, suggest that (V) contains only bridging trifluoroacetato-groups. The overlap of the bridging trifluoroacetato- and 2,2′-bipyridyl absorptions at *ca.* 1 600 cm^{-1} is an unfortunate confusion. However, a comparison of the spectrum (Figure 1e) with that for $[Mo_2(bipy)_2Cl_4]$ (Figure 1h) shows clearly that the absorption in the former at *ca.* 1 600 cm^{-1} is too broad and, relative to the absorptions at *ca.* 770 and 730 cm^{-1}, too intense to be due to 2,2′-bipyridyl alone. These latter considerations would also appear to apply to the i.r. spectra of (I)—(IV) (Figures 1a—d) and these, together with the absorptions at *ca.* 860, 780, and 735 cm^{-1}, are taken to indicate that each of the 1 : 1 and 1 : 2 adducts contain bridging trifluoroacetato-groups. The absorptions at 1 682, 825, 797, and 717 cm^{-1} of (III) suggest that, in addition to bridging trifluoroacetato-groups, ionic ones are also present. The (OCO) asymmetric stretching frequency regions for (I), (II), and (IV) are complicated and, in addition to bridging trifluoroacetato-groups, it is suggested that each compound contains two other types of trifluoroacetate group. The absorptions exhibited by (IV) at 1 681 and 1 704 cm^{-1} are attributed to ionic and unidentate trifluoroacetate groups, respectively. In the case of (I) the absorptions at 1 688 and 1 655 cm^{-1} are assigned to ionic and bidentate trifluoroacetate groups, respectively. The absorptions at 1 658 and 1 697 cm^{-1} for (II) are attributed to bidentate and unidentate trifluoroacetato-groups, respectively. The absence of an (OCO) deformation absorption at *ca.* 800 cm^{-1} shows very clearly that there are no ionic trifluoroacetate groups in (II).

In the light of the structural considerations presented for the 2,2′-bipyridyl and trifluoroacetate ligands in (I)—(V), and the geometry of the dimolybdenum(II) centre, it is possible to suggest certain structures for these compounds. If further assumptions are made, namely that only one type of dimolybdenum centre is present in each compound and that this contains a *cis*-bis(trifluoroacetato)-bridging unit, a unique structure appears to be indicated for each of the compounds, as shown in Figure 3.

Some comments are merited concerning the nature of the solutions from which the various adducts (I)—(IV) originate. No equilibrium solution species appears to be formed in the case of CCl_4. The compound (II) precipitates immediately upon mixing of a solution of 2,2′-bipyridyl and a finely divided suspension of $[Mo_2$-

$(O_2CCF_3)_4]$ (2 : 1) in this solvent. The product may, therefore, result from the approach of a 2,2′-bipyridyl ligand along an axial direction of $[Mo_2(O_2CCF_3)_4]$, the subsequent chelation of the addended ligand prompting a structural rearrangement of the bridging trifluoroacetato-framework. The insolubility of the 1 : 1 adduct in CCl_4 would effectively preclude any further reaction. Solutions of 2,2′-bipyridyl and $[Mo_2(O_2CCF_3)_4]$ (2 : 1) in CH_2Cl_2 (i) are very weakly conducting {for a 2×10^{-4}-M solution in $[Mo_2(O_2CCF_3)_4]$, $\Lambda_m = 2$ S cm^2 mol^{-1}}, (ii) contain free and co-ordinated 2,2′-bipyridyl in a ratio which does not appear to be very concentration dependent, as monitored by the absorption maxima at *ca.* 285 and 307 nm characteristic [9] of free and co-ordinated 2,2′-bipyridyl, respectively, and (iii) appear to involve unidentate but not bidentate or ionic trifluoroacetato-groups since the only major i.r. absorptions in the region 1 620—1 720 cm^{-1} occur at *ca.* 1 709 cm^{-1} (by contrast $[NEt_4][CF_3CO_2]$ in CH_2Cl_2 gives rise to an absorption at 1 687 cm^{-1}). It is suggested that all of these data are consistent with these CH_2Cl_2 solutions containing an equilibrium mixture which involves a small amount of the ionic structure [Figure 2, (I)] and a much larger amount of the covalent structure [Figure 2, (VI)], the former structure presumably being adopted in the solid phase due to its lower solubility. Compound (III) dissolves in acetone (see Scheme) to produce an equimolar mixture of (I) and $[Mo_2(O_2CCF_3)_4]$.

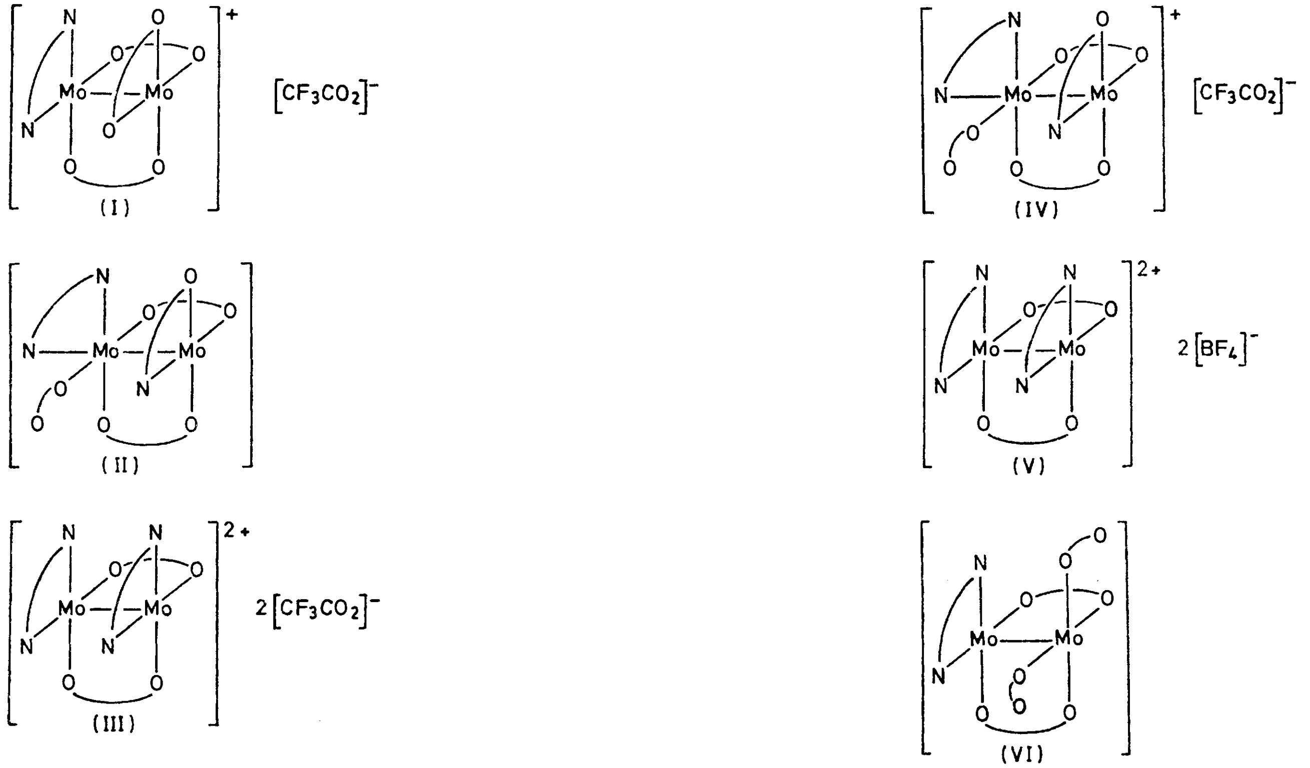

FIGURE 2 Suggested structures for $Mo_2(O_2CCF_3)_4$–2,2′-bipyridyl compounds

Mixtures of 2,2′-bipyridyl and $[Mo_2(O_2CCF_3)_4]$ (2 : 1) in ether do not appear to react for concentrations of the latter < *ca.* 10^{-3} mol l^{-1}. However, at concentrations of these reactants greater than the above value a reaction ensues with the immediate precipitation of (IV). It is not clear, either why a 2 : 1 adduct should be formed under these circumstances, or why any particular structure should be favoured.

Compound (III) is precipitated from reasonably concentrated solutions of $[Mo_2(O_2CCF_3)_4]$ and 2,2′-bipyridyl (1 : 2) in MeCN, EtOH, or Me_2CO. At concentrations less than that at which precipitation occurs, each of these solutions is conducting although the Λ_m value varies as 60, 26, and 12 S cm^2 mol^{-1} for MeCN, EtOH, and Me_2CO, respectively. The first of the solvents proved the most amenable for i.r. and electronic spectroscopic studies. The electronic spectra of solutions containing $[Mo_2(O_2CCF_3)_4]$ and 2,2′-bipyridyl (1 : 2) at various concentrations showed that the ratio of free to co-ordinated 2,2′-bipyridyl decreased with increasing concentration, until at a $[Mo_2]$ concentration of *ca.* 2×10^{-4} mol l^{-1}, no free 2,2′-bipyridyl could be detected and the electronic spectrum of the solution was virtually identical to that of (V). The i.r. spectra of these MeCN solutions (*ca.* 10^{-3} molar in $[Mo_2]$) between 1 620 and 1 720 cm^{-1} show only an absorption at 1 687 cm^{-1} which is very close to that (1 691 cm^{-1}) observed for $[NEt_4][CF_3CO_2]$ in this solvent, suggesting that only bridging and ionic trifluoroacetate groups can be present in these solutions. These data may be reconciled by assuming that the more concentrated solutions contain only species with the structure [Figure 2, (III)] suggested for the compound (III) which originates in these solutions. The rather low value of Λ_m can be attributed to extensive ionic association between the trifluoroacetate anions and the dipositive cation at the axial positions of the latter, in a manner directly analogous to that suggested for $[Re_2(O_2CPh)_4Cl_2]$ [13] and $[NEt_4][Mo_2(O_2CCF_3)_5]$.[1] The 'ionic' trifluoroacetate of this latter compound exhibits its (OCO) asymmetric stretching frequency at 1 692 cm^{-1} in MeCN. The variation of the electronic spectral data of these solutions suggests that a concentration-dependent equilibrium exists. At low concentrations the cation of the 2 : 1 electrolyte [Figure 2, (III)] is less favoured than one in which there are fewer co-ordinated 2,2'-bipyridyl groups and more trifluoroacetato-groups and/or some co-ordinated MeCN molecules. Electronic spectral studies also indicate that a similar concentration-dependent equilibrium probably is obtained in EtOH. However, the balance of the equilibrium is shifted relative to that in MeCN, since even at concentrations of 2×10^{-4} mol l^{-1} in $[Mo_2]$, the solutions contain free 2,2'-bipyridyl. Dissociation in this solvent would also appear to prevail at even higher concentrations since the average molecular weight of the solut on species formed by $[Mo_2(O_2CCF_3)_4]$ and 2,2'-bipyridyl (1 : 2) (0.075, 0.05, and 0.025 molar $[Mo_2]$) in EtOH was determined as 400 ± 20.

Although some rationalisation of the solution behaviour of the title reaction has been possible and it is seen that the more ionic solids are produced from the better ion-supporting media, the exact role of the solvent in determining the course and products of the reactions is still obscure. The increase in the 2,2'-bipyridyl $[Mo_2(O_2CCF_3)_4]$ ratio to values $>4:1$ does not change the nature of the products of these reactions. Therefore, substitution of more than two trifluoroacetato-groups appears to be resisted in a manner which resembles that noted [14] for $[Rh_2(O_2CCH_3)_4]$. It is this feature which prompted the earlier suggestion that the compounds isolated in this study contain the *cis*-dicarboxylatodimolybdenum(II) moiety. Such a feature may well be a persistent structural feature of substituted binuclear metal(II) carboxylates.

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