Molybdenum(II) Trifluoroacetate Dimer. Bispyridine Adduct[1]

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Abstract: The bispyridine adduct of molybdenum(II) trifluoroacetate dimer, $Mo_2(O_2CCF_3)_4(C_5H_5N)_2$, has been crystallized and its structure determined by X-ray crystallography for comparison with the known structure of $Mo_2(O_2CCF_3)_4$. Both compounds have the dinuclear, carboxylate-bridged configuration with Mo–Mo bond lengths of 2.129 (2) Å in the adduct and 2.090 (4) Å in the parent compound. The Mo–N distance in the adduct is 2.548 (8) Å, and the Mo–Mo–N angle is 171.0 (2)°. Other average intramolecular distances (and average esd's) include Mo–O = 2.116 (6), C–O = 1.26 (1), C–F = 1.29 (1), and O···O = 2.242 (9) Å. Implications of the small difference in Mo–Mo distance between the two compounds and the very long Mo–N bond are discussed. The Mo–Mo stretching frequency in the solid-state Raman spectrum of the adduct is 367 cm^{-1}, as compared to 397 cm^{-1} in the parent compound. The Mo–Mo stretching frequencies for $Mo_2(O_2CCF_3)_4$ in seven solvents are found to decrease from the solid-state value in a manner roughly correlated with increasing donor strength of the solvent. The lowest energy electronic transition for the compound follows the same pattern as a function of solvent. The adduct crystallizes in the triclinic space group $P\bar{1}$ with unit-cell dimensions a = 10.245 (8), b = 8.736 (7), c = 8.564 (8) Å; α = 85.538 (9), β = 101.923 (9), γ = 113.478 (1)°; V = 688 (3) $Å^3$; ρ_{calcd} = 1.94 (1) g/cm^3 for Z = 1; ρ_{obsd} = 1.90 (2) g/ml. The structure was determined from the diffractometer-measured intensities of 1131 unique reflections; it was solved by direct methods and refined by full-matrix least squares to a conventional R = 0.060 and weighted R = 0.053. The molecule lies on an inversion center in the crystal. There are no significant intermolecular contacts. The preparation of rhodium(II) benzoate and unsuccessful attempts to crystallize dinuclear rhodium(II) and chromium(II) carboxylates without axial donors are also described.

The strongest known metal–metal bonds among the transition elements are found in a series of dinuclear compounds with formally anionic ligands, namely carboxylate, halide, alkyl, and allyl groups. Excepting the allyls,[3] these compounds all have high idealized symmetry, usually D_{4h},[4] as represented by the carboxylate structure shown in Figure 1. Elimination of the axial ligands L and replacement of each carboxylate by two halide or alkyl groups give the corresponding compounds of those classes, examples of which are $Re_2Br_8^{-2}$[5] and $Cr_2(CH_3)_8^{4-}$.[6] The high symmetry makes feasible a meaningful qualitative treatment of the *possibilities* for metal–metal bonding in such compounds,[7] the conclusion being that the strongest bonds within a given transition-metal row should occur for the d^4 electronic configuration (*e.g.*, Cr^{II}, Mo^{II}, Re^{III}). This is borne out by the available X-ray data on dinuclear carboxylates, summarized in Table I. The carboxylates are by far the most numerous compounds of this type; indeed they are the only ones for which appreciable structural data are available for other than d^4 metals.

We have been interested for some time in the general question of how metal–metal bond strength in these compounds is affected by the more important variables in the system, namely, the position of the metal in the periodic table,[3,8–14] the nature of the anionic ligands,[15] and, in the case of the carboxylates, the nature of the axial donor ligands L. The last question is a particularly important one, since the presence of different axial ligands in the known carboxylate structures complicates any attempt to answer unambiguously the first two questions using these structures. Direct comparisons between carboxylates with and without axial ligands are needed to resolve this ambiguity. We have obtained the first such comparison by preparing and determining the crystal and molecular structures of the bispyridine adduct of dinuclear molybdenum(II) trifluoroacetate, for comparison with those of $Mo_2(O_2CCF_3)_4$ which we determined previously.[15] This paper

Table I. Interatomic Distances in Dinuclear Carboxylates

Electronic configuration	Compound	M–M, Å	M–L, Å
	First Row		
d^4	$Cr_2(OAc)_4(H_2O)_2$[a]	2.362 (1)	2.272 (3)
d^9	$Cu_2(OAc)_4(py)_2$[d]	2.630 (3)	2.13 (1)
	Second and Third Rows		
d^4	$Mo_2(OAc)_4$[e]	2.11 (1)	
	$Mo_2(O_2CCF_3)_4$[f]	2.090 (4)	
	$Re_2(O_2CPh)_4Cl_2$[b]	2.235 (2)	2.489 (5)
$d^{5.5}$	$Ru_2(O_2CC_3H_7)_4Cl$[c]	2.281 (4)	2.587 (5)
d^7	$Rh_2(OAc)_4(H_2O)_2$[a]	2.386 (1)	2.310 (3)

[a] Reference 8. [b] Reference 9. [c] Reference 10. [d] Reference 13. [e] Reference 14. [f] Reference 15.

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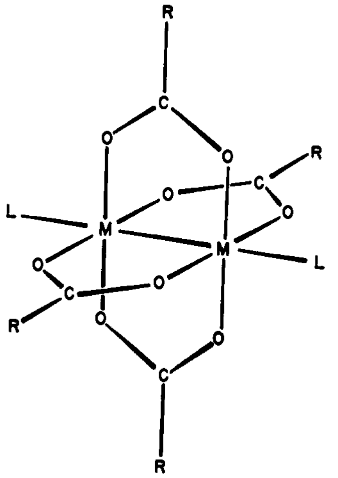

Figure 1. The general structure adopted by the compounds of formula $M_2(O_2CR)_4L_2$, M = Cr, Mo, Re, Ru, Rh, Cu.

summarizes the results of that investigation and related experiments. Unsuccessful attempts to crystallize rhodium(II) and chromium(II) carboxylates without axial ligands are also described.

Experimental Section

Preparation of $Mo_2(O_2CCF_3)_4(py)_2$. All manipulations were carried out in an atmosphere of dry nitrogen or argon. Reagent-grade solvents were degassed by alternate freezing and thawing *in vacuo* and dried over molecular sieves before use.

$Mo_2(O_2CCF_3)_4$[15] (0.6 g) was warmed with stirring in 6 ml of pyridine to give a red solution, which solidified to a gel upon cooling to −20°. The gel was transferred to a Schlenk filter and washed extensively with pentane to give a yellow-orange powder. The powder was redissolved in 10 ml of CH_2Cl_2 and the orange solution was filtered. Cooling at −20° for several hours gave well-formed orange crystals. Excess solvent was decanted and the crystals were washed with several 5-ml portions of pentane and dried in a slow stream of nitrogen or argon. They were stored under nitrogen or argon at −20°; under these conditions they appear to be stable indefinitely, yield 0.5 g (70%).

Anal. Calcd for $C_{18}H_{10}F_{12}Mo_2N_2O_8$: C, 26.95; H, 1.26; F, 28.42; Mo, 23.92; N, 3.49. Found: C, 26.87; H, 1.40; F, 28.51; Mo, 23.90; N, 3.58. Elemental analyses were obtained from Meade Microanalytical Laboratory, Amherst, Mass.

Ir spectrum (fluorolube and Nujol mulls, 4000–400 cm^{-1}): 3075 w, 3030 w, 2890 m, 1615 s, 1605 s, 1495 m, 1455 s, 1195 br, 1165 br, 1070 s, 1034 s, 1002 s, 854 s, 777 s, 748 s, 728 s, 697 s, 676 w, 615 s, 523 m, 511 m, 491 m cm^{-1}.

Raman and Electronic Spectra. Raman spectra of $Mo_2(O_2CCF_3)_4$ in seven solvents and of $Mo_2(O_2CCF_3)_4(py)_2$ and $Mo_2(OAc)_4(py)_2$ in the solid state were obtained from 200 to 600 cm^{-1} using a Cary-81 spectrometer with a Spectra-Physics helium-neon laser as the source of 6328-Å exciting radiation. The solution frequencies obtained are accurate to ±2 cm^{-1} and the solid-state frequencies to ±4 cm^{-1}. Electronic spectra of $Mo_2(O_2CCF_3)_4$ in the same solvents used for the Raman experiments were obtained from 14 to 25 kK using a Cary-14 spectrometer. All spectral measurements were made in an atmosphere of nitrogen or argon, and solvents were degassed and dried over molecular sieves before use.

Collection and Reduction of X-Ray Data. Crystals of $Mo_2(O_2CCF_3)_4(py)_2$ are approximately, but never exactly, hexagonal; they were sealed in Lindemann glass capillaries under argon for X-ray work. Despite this precaution, the crystals decomposed slowly, and it was necessary to use three for the collection of intensity data in addition to one for preliminary photographic work.

Weissenberg (*hk*0, *hk*1, *hk*3) and precession (*h*0*l*, 0*kl*) photographs using Cu Kα and Mo K$\bar{\alpha}$ radiation, respectively, suggested triclinic symmetry, implying space groups $P1$ (C_1^1, no. 1) or $P\bar{1}$ (C_i^1, no. 2). Intensity data were collected on a General Electric XRD-5 manual diffractometer using Nb-filtered Mo Kα radiation (λ = 0.71069 Å). Each of the three crystals used was aligned so that c^* was coincident with the φ axis, and unit-cell dimensions were determined by least-squares refinement based on the accurately measured settings of 16 reflections. The three sets of unit-cell parameters were not significantly different within the esd's assigned by the least-squares process; weighted mean values and esd's, where the weights are the fraction of reflections collected with each crystal, are a = 10.245 (8), b = 8.736 (7), c = 8.564 (8) Å; α = 85.538 (9), β = 101.923 (9), γ = 113.478 (1)°; V = 688 (3) Å^3. These values lead to ρ_{calcd} = 1.94 (1) g/cm^3 for $Z = 1$; ρ_{obsd} = 1.90 (2) g/ml (flotation, CH_2BrCH_2Br–heptane). With $Z = 1$ the molecule must lie on an inversion center in $P\bar{1}$. The dimensions of each crystal were carefully measured and the major faces identified from their diffraction positions as (100), ($\bar{1}$00), (010), (0$\bar{1}$0), (1$\bar{1}$0), ($\bar{1}$10), (001), and (00$\bar{1}$).

Intensities were measured using a scintillation counter; the takeoff angle was 2° and the pulse-height analyzer was set to admit 95% of the Mo Kα peak. Peak counts P were accumulated using θ–2θ scans with a scan rate of 4°/min and a fixed scan width of 2.66°. Background counts B_1 and B_2 were taken for 20 sec at each end of the scan range. Three reflections (040, $\bar{3}$04, 002) were remeasured at regular intervals throughout data collection; a steady decrease in intensity with time, linear and uniform over the three reflections within the limits imposed by counting statistics and an assumed 3% machine error, was observed for each crystal; a particular crystal was discarded when the intensity drop reached 11–14%. The final data set consisted of 1131 unique reflections, complete in the range 2θ = 0–35°, and including all (*nh*, *nk*, *nl*), that is, index sets with a common divisor, in the range 2θ = 35–50°.

Statistical analysis of the data showed that more than half had $I > 2\sigma_I$, where $I = P - B_1 - B_2$ and $\sigma_I = (P + B_1 + B_2)^{1/2}$, in every 5° interval of 2θ; hence all reflections were accepted, those with $I < \sigma_I/2$ being assigned $I = \sigma_I/2$. The intensities were converted to structure factor amplitudes, $|F_o| = (I/Lp)^{1/2}$, where $Lp = (1 + \cos^2 2\theta)/\sin 2\theta$, and their esd's, $\sigma_F = (4ILp)^{-1/2}[\sigma_I^2 + (0.3I)^2]^{1/2}$. The data for each crystal were corrected for decomposition using a linear least-squares analysis of the plot of check reflection intensity *vs.* time. The three data subsets were scaled together approximately using the intensities of 25 common reflections; in addition, a separate scale factor was applied to each subset in the least-squares refinement of the structure. The original I/σ_I ratios were maintained in making the decomposition and scaling corrections.

Solution and Refinement. Atomic scattering factors used were those of Cromer and Waber.[16] All were corrected for anomalous dispersion using the values of $\Delta f'$ and $\Delta f''$ given by Cromer and Liberman.[17]

The structure was solved in $P\bar{1}$ by the symbolic addition procedure.[18] Normalized structure factors were calculated by the relationship $E^2 = |F_o|^2 \exp 2Bp^2/\epsilon k^2 \Sigma f_i^2$, where $p = \sin\theta/\lambda$, B = overall temperature factor, k = overall scale factor between $|F_o|$ and $|F_c|$, ϵ = integer to correct for extinct reflections in special zones, and f_i = scattering factor for atom i. B and k were obtained from a Wilson plot. The phases of 314 of the 400 largest E's were determined in terms of seven symbols by an iterative process. The probability level required for phase determination was 0.995, and no inconsistencies were allowed. One particular combination of signs for the symbols was uniquely favored over all other possibilities.

An E map was computed using the most probable sign combination and from it unambiguous positions were derived for 15 of the 21 nonhydrogen atoms in the asymmetric unit $Mo(O_2CCF_3)_2(C_5H_5N)$. Three cycles of least-squares refinement using isotropic temperature factors for all atoms gave $R_1 = \Sigma||F_o| - |F_c||/\Sigma|F_o| = 0.213$ and $R_2 = \Sigma w_F||F_o| - |F_c||^2/\Sigma w_F|F_o|^2 = 0.271$, where the weights are $w_F = \sigma_F^{-2}$. A difference Fourier synthesis yielded reasonable positions for the remaining six nonhydrogen atoms; three cycles of refinement gave R_1 = 0.126 and R_2 = 0.137.

The data for each crystal were corrected separately for absorption (μ = 10.31 cm^{-1}); the largest range of calculated transmission factors was for crystal no. 2, 0.876–0.942, or ±3.6% around the mean. Two cycles of isotropic refinement on the corrected data gave R_1 = 0.124 and R_2 = 0.135. All atoms were now given anisotropic thermal parameters; two cycles of refinement gave R_1 = 0.061, R_2 = 0.059.

An empirical weighting scheme was introduced to remove an observed dependence of the quantity $w_F||F_o| - |F_c||^2$ on $\lambda^{-1} \sin\theta$ and $|F_o|$, in accordance with Cruickshank's cri-

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Table II

Final Positional and Thermal Parameters[a]

Atom	*X*	*Y*	*Z*	*B*,[b] Å^2
Mo	0.09494 (8)	−0.0243 (1)	0.0439 (1)	3.99 (5)
F(1)	−0.073 (1)	0.224 (1)	0.4640 (9)	10.6 (5)
F(2)	0.121 (1)	0.400 (1)	0.408 (1)	13.1 (6)
F(3)	0.1185 (8)	0.1908 (9)	0.5499 (7)	8.3 (4)
F(4)	0.200 (1)	0.545 (1)	−0.249 (1)	12.9 (6)
F(5)	0.326 (2)	0.570 (1)	−0.023 (1)	16.3 (8)
F(6)	0.368 (1)	0.478 (1)	−0.206 (1)	13.1 (7)
O(1)	0.1225 (7)	0.0918 (8)	0.2646 (7)	4.8 (3)
O(2)	−0.0789 (7)	0.1391 (7)	0.1695 (7)	4.9 (3)
O(3)	0.2307 (6)	0.2098 (8)	−0.0335 (7)	5.0 (3)
O(4)	0.0318 (7)	0.2636 (7)	−0.1245 (7)	5.0 (3)
N	0.3153 (9)	−0.078 (1)	0.193 (1)	5.7 (5)
C(1)	0.029 (1)	0.147 (1)	0.274 (1)	4.5 (5)
C(2)	0.053 (1)	0.246 (2)	0.425 (1)	5.8 (6)
C(3)	0.167 (1)	0.304 (1)	−0.097 (1)	4.8 (6)
C(4)	0.259 (1)	0.476 (2)	−0.138 (2)	7.2 (7)
C(5)	0.448 (1)	0.034 (2)	0.180 (1)	7.4 (7)
C(6)	0.572 (1)	0.016 (2)	0.266 (2)	9.0 (9)
C(7)	0.559 (2)	−0.120 (2)	0.363 (2)	8.9 (9)
C(8)	0.423 (2)	−0.235 (2)	0.372 (2)	9.1 (8)
C(9)	0.304 (1)	−0.207 (2)	0.384 (1)	6.9 (6)

Anisotropic Thermal Parameters,[c] Å^2

Atom	B_{11}	B_{22}	B_{33}	B_{12}	B_{13}	B_{23}
Mo	3.02 (5)	4.55 (5)	4.30 (5)	1.81 (3)	0.01 (3)	0.60 (3)
F(1)	9.4 (5)	17.3 (8)	7.7 (4)	7.7 (5)	0.8 (4)	−2.8 (4)
F(2)	21 (1)	5.4 (4)	9.0 (5)	0.9 (5)	3.4 (5)	−1.1 (3)
F(3)	9.8 (4)	10.7 (5)	5.2 (3)	5.7 (4)	−0.4 (3)	−0.8 (3)
F(4)	10.5 (5)	6.8 (4)	16.5 (7)	0.9 (4)	−0.7 (5)	5.4 (5)
F(5)	22 (1)	6.7 (4)	10.6 (6)	−4.4 (6)	2.8 (6)	−1.1 (4)
F(6)	10.2 (6)	8.7 (5)	19 (1)	1.2 (4)	6.2 (6)	4.4 (6)
O(1)	3.8 (3)	5.5 (3)	5.0 (3)	2.2 (3)	−0.4 (2)	0.1 (2)
O(2)	4.3 (3)	5.7 (3)	5.1 (3)	2.8 (2)	0.4 (3)	0.5 (3)
O(3)	3.5 (3)	5.3 (3)	5.4 (3)	1.3 (3)	0.7 (2)	0.6 (3)
O(4)	4.4 (3)	4.7 (3)	5.5 (3)	2.1 (2)	−0.4 (3)	0.7 (2)
N	4.0 (5)	6.9 (5)	6.3 (5)	2.9 (4)	0.0 (3)	0.9 (4)
C(1)	4.0 (5)	4.1 (4)	5.4 (6)	1.8 (4)	1.2 (4)	1.6 (4)
C(2)	6.4 (7)	6.8 (7)	4.5 (6)	3.1 (6)	0.3 (5)	−0.3 (5)
C(3)	4.8 (6)	4.5 (5)	4.6 (5)	1.7 (5)	0.0 (4)	0.9 (4)
C(4)	5.8 (7)	5.6 (7)	7.6 (7)	0.9 (6)	−1.3 (6)	0.3 (7)
C(5)	3.5 (5)	8.9 (8)	8.6 (7)	1.6 (6)	0.5 (5)	0.8 (6)
C(6)	4.0 (7)	10 (1)	12 (1)	1.9 (6)	−0.2 (6)	0.6 (8)
C(7)	6.9 (9)	8.6 (9)	12 (1)	4.5 (8)	0.6 (7)	0.0 (8)
C(8)	6.6 (8)	8.7 (8)	11 (1)	3.8 (7)	−0.7 (7)	2.3 (7)
C(9)	5.3 (6)	6.7 (6)	8.6 (7)	3.0 (5)	0.1 (5)	1.8 (6)

[a] Numbers in parentheses represent esd's in the last figure quoted for all tables. [b] Effective isotropic *B*'s for the anisotropically refined atoms. [c] The form of the temperature factor expression is $\exp[-{}^1/_4(B_{11}h^2a^{*2} + B_{22}k^2b^{*2} + B_{33}l^2c^{*2} + 2B_{12}hka^*b^* + 2B_{13}hla^*c^* + 2B_{23}\cdot klb^*c^*)]$.

terion;[19] inspection of the data indicated that the dependence did not result from secondary extinction. Two cycles of refinement using the new weights gave $R_1 = 0.060$, $R_2 = 0.053$ as final values. The esd of a unit-weight observation was 1.06, and $w_F||F_o| - |F_c||^2$ was now essentially independent of both $\lambda^{-1} \sin \theta$ and $|F_o|$, indicating the correctness of the weighting scheme. A difference Fourier synthesis was computed using the final parameters; the largest peak, in the vicinity of the molybdenum atom, had a density of 1.18 e/Å^3. No attempt was made to locate hydrogen atoms.

The effects of all correlation coefficients ≥0.2 between positional parameters from the final correlation matrix were included in calculating esd's for interatomic distances and angles, as well as correlations due to nonorthogonality of cell axes and those between unit-cell parameters.

Computer Programs. Programs used in the structure determination were as given previously.[15]

Preparation of Rhodium(II) Benzoate. Under nitrogen 0.5 g of $Rh_2(OAc)_4$[20] and 5 g of benzoic acid were heated together until the acid melted. The solution was stirred 5 min and cooled to room temperature. The solid melt was ground to a powder and washed extensively with a 1:1 mixture of Et_2O and CCl_4 to remove excess acid. The green solid was redissolved in boiling acetone and the blue solution was cooled at −20° overnight. The blue crystals of the *acetone adduct* were filtered and dried in a slow stream of nitrogen.

Anal. Calcd for $Rh_2(O_2CPh)_4(Me_2CO)_2$: C, 50.6; H, 4.00. Found: C, 50.4; H, 3.93.

Ir spectrum (fluorolube and Nujol mulls, 4000–400 cm^{-1}): 3055 w, 2905 w, 1680 s, 1600 s, 1560 s, 1445 m, 1400 s, 1237 m, 1181 m, 1176 m, 1157 w, 1141 w, 1088 w, 1070 m, 1025 s, 1000 w, 989 w, 973 w, 943 s, 807 w, 712 s, 692 s, 552 m, 518 s cm^{-1}.

The adduct was heated at 100° *in vacuo* for 2 hr to give unsolvated rhodium(II) benzoate as a green solid. The compound is stable to water and air, yield 0.7 g (90%).

Anal. Calcd for $Rh_2(O_2CPh)_4$: C, 48.72; H, 2.92. Found: C, 48.74; H, 3.13.

Ir spectrum: 3055 w, 1595 s, 1550 s, 1500 m, 1445 m, 1400 s, 1177 m, 1157 w, 1142 m, 1069 m, 1029 s, 1000 w, 975 w, 931 m, 855 m, 842 s, 804 w, 727 s, 708 s, 692 s, 524 s, 515 s.

Pmr spectrum (acetone-d_6): complex multiplets, τ 2.17 and 2.73, intensities 2 and 3, respectively. The similarity of this spectrum to that of benzoic acid suggests that the compound, like $Rh_2(OAc)_4$, is diamagnetic.

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Table III. Intramolecular Distances, Å

Mo–Mo	2.129 (2)	C(2)–F(1)	1.33 (1)	O1···O2	2.242 (9)
Mo–N	2.548 (8)	C(2)–F(2)	1.25 (1)	O3···O4	2.243 (9)
Mo–O(1)	2.128 (6)	C(2)–F(3)	1.31 (1)	F1···F2	2.09 (1)
Mo–O(2)	2.098 (6)	C(4)–F(4)	1.27 (1)	F1···F3	2.07 (1)
Mo–O(3)	2.111 (6)	C(4)–F(5)	1.23 (2)	F2···F3	2.11 (1)
Mo–O(4)	2.125 (6)	C(4)–F(6)	1.35 (2)	F4···F5	2.06 (2)
C(1)–O(1)	1.25 (1)	N–C(5)	1.34 (1)	F4···F6	1.99 (1)
C(1)–O(2)	1.25 (1)	N–C(9)	1.31 (2)	F5···F6	2.01 (2)
C(3)–O(3)	1.27 (1)	C(5)–C(6)	1.40 (2)		
C(3)–O(4)	1.26 (1)	C(6)–C(7)	1.37 (2)		
C(1)–C(2)	1.54 (2)	C(7)–C(8)	1.37 (2)		
C(3)–C(4)	1.49 (2)	C(8)–C(9)	1.40 (2)		

Table IV. Intramolecular Angles, Deg

Mo–Mo–O(1)	90.0 (2)	Mo–O(1)–C(1)	115.5 (6)	F(1)–C(2)–F(2)	108 (1)
Mo–Mo–O(2)	93.1 (2)	Mo–O(2)–C(1)	114.0 (7)	F(1)–C(2)–F(3)	103.1 (9)
Mo–Mo–O(3)	92.3 (2)	Mo–O(3)–C(3)	115.2 (6)	F(2)–C(2)–F(3)	111 (1)
Mo–Mo–O(4)	90.8 (2)	Mo–O(4)–C(3)	116.3 (6)	F(4)–C(4)–F(5)	111 (1)
Mo–Mo–N	171.0 (2)	Mo–N–C(5)	118.6 (8)	F(4)–C(4)–F(6)	99 (1)
O(1)–Mo–O(2)	176.9 (3)	Mo–N–C(9)	122.3 (7)	F(5)–C(4)–F(6)	102 (1)
O(3)–Mo–O(4)	176.9 (3)	O(1)–C(1)–O(2)	127 (1)	C(5)–N–C(9)	119 (1)
O(1)–Mo–O(3)	87.9 (2)	O(3)–C(3)–O(4)	125.2 (9)	N–C(5)–C(6)	121 (1)
O(2)–Mo–O(4)	87.8 (2)	O(1)–C(1)–C(2)	117.2 (9)	C(5)–C(6)–C(7)	120 (1)
O(1)–Mo–O(4)	92.7 (2)	O(2)–C(1)–C(2)	115 (1)	C(6)–C(7)–C(8)	119 (1)
O(2)–Mo–O(3)	91.5 (2)	O(3)–C(3)–C(4)	117 (1)	C(7)–C(8)–C(9)	118 (1)
N–Mo–O(1)	81.6 (3)	O(4)–C(3)–C(4)	117.7 (9)	C(8)–C(9)–N	123 (1)
N–Mo–O(2)	95.3 (3)	C(1)–C(2)–F(1)	111 (1)		
N–Mo–O(3)	90.7 (3)	C(1)–C(2)–F(2)	112.0 (9)		
N–Mo–O(4)	86.3 (3)	C(1)–C(2)–F(3)	111 (1)		
		C(3)–C(4)–F(4)	116 (1)		
		C(3)–C(4)–F(5)	115 (1)		
		C(3)–C(4)–F(6)	112 (1)		

Table V. Weighted Least-Squares Planes[a]

Plane	Equation	Angles between planes, deg
1. $O_1O_2C_1C_2$	$-0.6321x - 0.6557y + 0.4130z = 0.1523$	79 (1)
2. $O_3O_4C_3C_4$	$-0.1203x + 0.3983y + 0.9093z = -0.1777$	89 (1) 88 (1)
3. $O_1O_3O_2'O_4'$	$0.7595x - 0.5320y + 0.3743z = 1.1206$	90 (1) 15 (1)
4. $NC_5C_6C_7C_8C_9$	$-0.1556x + 0.6218y + 0.7675z = -0.3200$	

Distances of Atoms from Planes,[b] Å

1. O_1, −0.004; O_2, −0.004; C_1, 0.02; C_2, −0.02; Mo, −0.1449; Mo′, −0.1597
2. O_3, 0.001; O_4, 0.001; C_3, −0.01; C_4, 0.01; Mo, 0.1862; Mo′, 0.1692
3. O_1, −0.000; O_3, 0.000; O_2, −0.000; O_4, 0.000; Mo, −0.0565
4. N, 0.004; C_5, −0.01; C_6, 0.01; C_7, 0.00; C_8, −0.01; C_9, 0.00; Mo, 0.1200

[a] The orthogonal coordinates (x, y, z) are directed along the crystal axes ($b \times c^*$, b, c^*), respectively, and are in ångströms. The weight given each atom i in forming the planes is $w_i = [a\sigma_{xi}b\sigma_{yi}c\sigma_{zi}]^{-2/3}$. Primed atoms are related by an inversion center to those in the atom parameter table. [b] Average esd's of atomic positions are (Å): Mo, 0.0008; O, 0.007; N, 0.009; C, 0.01.

$Rh_2(O_2CR)_4$ (R = CCl_3, CF_3, CF_2H, CFH_2, C_3H_7) and $Cr_2(O_2CCF_3)_4$ are readily prepared from $Rh_2(OAc)_4$ or $Cr_2(OAc)_4$ by modifications of the above carboxylate exchange procedure. The first two have been reported;[21-23] rhodium(II) benzoate has been previously obtained only as the triphenylphosphine and pyridine adducts.[20] A kinetic study of the rhodium(II) carboxylate exchange reaction has recently appeared.[24]

Results and Description of Structure

The final values of $|F_c|$ and $|F_o|$ scaled to $|F_c|$ appear in the microfilm edition of this journal.[25] Fractional coordinates and thermal parameters for the 21 unique atoms appear in Table II. Tables III–V present data on intramolecular distances, angles, and least-squares planes, respectively. Table VI contains the Raman and electronic spectral data. Figure 2 depicts the molecular structure and illustrates the atom numbering scheme.

As anticipated, $Mo_2(O_2CCF_3)_4(py)_2$ contains symmetrically bridging trifluoroacetate groups and a pyridine molecule coordinated to each metal atom opposite the metal–metal bond. The molecule lies on an inversion center in the crystal; hence only the unit $Mo(O_2CCF_3)_2(C_5H_5N)$ is crystallographically unique.

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(24) J. L. Bear, J. Kitchens, and M. R. Wilcott, *J. Inorg. Nucl. Chem.*, 33, 3479 (1971).

(25) A structure factor table will appear following these pages in the microfilm edition of this volume of the journal. Single copies may be obtained from the Business Operations Office, Books and Journals Division, American Chemical Society, 1155 Sixteenth St., N.W., Washington, D. C. 20036, by referring to code number JACS-72-5697. Remit check or money order for $3.00 for photocopy or $2.00 for microfiche.

Table VI

Solid-State Raman Spectra of Molybdenum Carboxylates

Compound	ν(Mo–Mo), cm^{-1}
$Mo_2(O_2CCF_3)_4$	397[a]
$Mo_2(O_2CCH_3)_4$	406[a]
$Mo_2(O_2CCF_3)_4(py)_2$	367
$Mo_2(O_2CCH_3)_4(py)_2$	363

Raman and Electronic Spectra of $Mo_2(O_2CCF_3)_4$ in Solution

Solvent[b]	ν(Mo–Mo), cm^{-1}	ν_{max}, kK
CH_2Cl_2	397	23.3
Benzene	390	23.2
Acetone	385	23.0
Ether	383[a]	22.9
Methanol	383	22.9
Et_3N	370	c
Pyridine	343	19.7

[a] Reference 15. [b] 0.05–0.50 *M* solutions. [c] A reliable value could not be obtained due to solvent absorption.

The two CCO_2 groups, the O_4 coordination set around the molybdenum atom, and the pyridine ring are each planar within experimental error. The metal atom lies in none of these planes, being drawn inward from the O_4 set by 0.057 Å to give a very short Mo–Mo distance of 2.129 (2) Å, comparable to the average Mo–O distance of 2.116 (6) Å. The long Mo–N distance of 2.548 (8) Å indicates a quite weak bonding interaction; it may be compared with the average Mo–O separation or the $M\text{–}OH_2$ distances in $M_2(OAc)_4(H_2O)_2$, M = Cr, Rh, which are 2.272 (3) and 2.310 (3) Å, respectively.[8] Other average interatomic distances (and average esd's) include C–O = 1.26 (1), C–F = 1.29 (1), C–C(py) = 1.38 (2), and F···F = 2.06 (1) Å. The carboxylate planes lie 79(1)° from each other and are essentially perpendicular to the O_4 plane; the pyridine plane lies much closer to one carboxylate (15°) than the other (90°). The Mo–Mo–N system is not exactly linear, L(Mo–Mo–N) being 171.0 (2)°. There are no intermolecular contacts significantly shorter than van der Waals radii.

The large anisotropy among the fluorine thermal parameters (Table II) and the direction of this anisotropy (Figure 2) suggest a slight rotational disorder in the CF_3 groups. This appears to be a relatively common phenomenon.[15]

Discussion

Synthesis. The bispyridine adducts of molybdenum(II) acetate and benzoate dimers[26] are the only previously reported well-characterized molybdenum carboxylates containing axial donor ligands; the normal synthetic procedures for the molybdenum system[15,26] lead to unsolvated compounds. By contrast, dinuclear carboxylates of other metals have been crystallized only *with* axial donors (see Table I) and in general appear to bind such donors, even very weak ones, if they are present in a given reaction mixture. Our initial approach to studying the effect of axial donors on the metal–metal bond strength involved attempts to crystallize unsolvated chromium(II) or rhodium(II) carboxylates from noncoordinating solvents. The most obvious choices in these systems, unsolvated chromium(II) and rhodium(II) acetates, are insoluble in such solvents. However, using the ligand exchange reaction described in detail for rhodium(II) benzoate in the Experimental Section, we were able to obtain a number of carboxylates of the two metals sufficiently soluble to allow crystallization to be attempted. Unfortunately crystals of the unsolvated compounds, when obtained, were invariably fragile and macroscopically twinned, precluding their use for a structural determination.

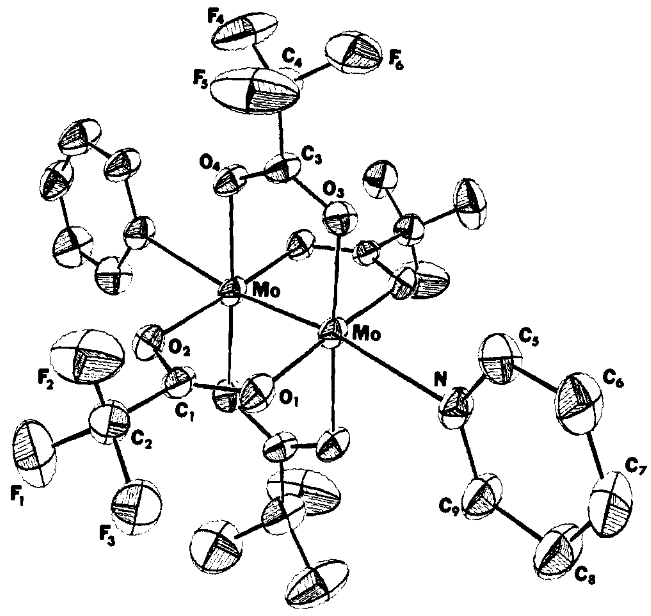

Figure 2. A perspective view of the molecular structure. The ellipsoids enclose 25% probability of thermal motion.

We next turned to molybdenum(II) carboxylates, where the problem is to crystallize a stable *solvated* compound. The previously reported pyridine adduct of molybdenum(II) acetate[26] was investigated, but it forms crystals of poor quality from pyridine and is insoluble in other solvents. However, the corresponding trifluoroacetate adduct was readily prepared and excellent crystals were obtained from CH_2Cl_2.

Raman and Electronic Spectra. Evidence that the metal–metal bond strength in $Mo_2(O_2CCF_3)_4(py)_2$ did differ significantly from that in $Mo_2(O_2CCF_3)_4$ was obtained from comparison of the Mo–Mo stretching frequencies in the Raman spectra of the two compounds. As can be seen from Table VI, the A_{1g} mode which most closely corresponds to pure metal–metal stretching[27] lies at 367 cm^{-1} in the pyridine adduct, 30 cm^{-1} below its value of 397 cm^{-1} in the unsolvated compound. It is interesting to note that the frequencies in the pyridine adducts of $Mo_2(OAc)_4$ and $Mo_2(O_2CCF_3)_4$ are essentially the same, just as is the case for the two unsolvated compounds. X-Ray structures of $Mo_2(OAc)_4$[14] and $Mo_2(O_2CCF_3)_4$[15] have confirmed that the Mo–Mo bond lengths are the same within the experimental uncertainties.

A weaker metal–metal bond, as indicated by the lowering of the Mo–Mo stretching frequencies, might be expected in the pyridine adducts, since the axial donors share the same metal orbitals as those used to form the σ component of the Mo–Mo bond. Hence to first order the metal–metal bond should progressively

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

[27] W. K. Bratton, F. A. Cotton, M. Debeau, and R. A. Walton, *J. Coord. Chem.*, 1, 121 (1971).

weaken as the metal-to-axial ligand bond strengthens. This idea is supported by the Mo–Mo stretching frequencies of $Mo_2(O_2CCF_3)_4$ in various solvents, given in Table VI. The frequencies decrease from the solid-state value in a manner roughly correlated with increasing donor strength of the solvent. The decrease for pyridine is by far the largest, and since the thermal stability of the crystalline pyridine adduct at room temperature is marginal, it seems doubtful that adducts containing weaker donors can be isolated under normal circumstances.

The frequency of the lowest energy electronic transition in $Mo_2(O_2CCF_3)_4$ appears to follow the same pattern as a function of solvent as the metal–metal stretching frequency (see Table VI). This observation has potential importance in the assignment of this transition, but we would not care to assess its significance without the aid of single-crystal polarized spectra. The two higher energy transitions[15] could not be studied as a function of solvent due to solvent absorption.

Molecular Structure. Comparison of the structure of $Mo_2(O_2CCF_3)_4(py)_2$ with the previous results for $Mo_2(O_2CCF_3)_4$[15] provides a quantitative measure of the decrease in Mo–Mo bond strength upon coordination of pyridine as an axial donor. The 2.129 (2) Å Mo–Mo bond length in the adduct is 0.039 (6) Å greater than the value of 2.090 (4) Å obtained for the parent compound. The difference is statistically significant but rather small from a chemical viewpoint. This coupled with the extremely long Mo–N bond of 2.548 (8) Å, 0.43 (1) Å longer than the average Mo–O distance, clearly indicates that the two molybdenum atoms energetically prefer to maintain their very strong metal–metal interaction rather than trade any significant amount thereof for a normal strength metal–ligand bond, *no matter how effective a donor the axial ligand L may be.* That is, the intrinsically strong Mo–Mo bond necessitates an intrinsically weak Mo–L bond. This "metal–metal *trans* effect" operates to some extent in the other dinuclear carboxylates. Thus, in $Cr_2(OAc)_4(H_2O)_2$[8] and $Cr_3O(OAc)_6(H_2O)_3^+$,[28] the average Cr–OAc distances of 2.018 (2) and 1.98 (1) Å are comparable to each other and to the Cr–OH_2 distance in the trimer, 2.02 (1) Å, but all are significantly shorter than the Cr–OH_2 distance in the dimer, 2.272 (3) Å. In the dimer, the water molecule is trans to the Cr–Cr bond; in the trimer, to the Cr–O bond. Again, the Rh–OH_2 distance of 2.310 (3) Å in $Rh_2(OAc)_4(H_2O)_2$ is substantially greater than the average Rh–OAc distance of 2.039 (2) Å. Nowhere is the trans effect more dramatically illustrated than in the molybdenum system, however; therefore, Mo(II) appears to have an intrinsically greater metal–metal bonding tendency in the carboxylate framework than do Cr(II) and Rh(II). This has long been suggested from theoretical considerations and the available X-ray data,[7] but never so conclusively demonstrated. One expects, then, that if good crystals of unsolvated $M_2(O_2CCF_3)_4$, M = Cr, Rh, could be obtained, which may not be possible, the Cr–Cr and Rh–Rh distances would definitely be longer than the Mo–Mo distance in $Mo_2(O_2CCF_3)_4$, allowing for differences in covalent radii. Moreover, if crystalline $M_2(O_2CCF_3)_4(py)_2$, M = Cr, Rh, could be obtained, which should be possible, the metal–nitrogen distances should definitely be shorter than in $Mo_2(O_2CCF_3)_4(py)_2$, again allowing for differences in covalent radii. The lengths found for metal-to-axial ligand bonds in the carboxylates thus provide valuable information about the implicit tendencies of the metals toward mutual attraction.

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Nuclear Magnetic Resonance Study of the Conformational Preferences of Some Substituted Ditertiary Arsine Chelate Complexes of Chromium Carbonyl[1,2]

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Abstract: The synthesis of some novel ditertiary arsine chelate complexes of chromium carbonyl are described. Detailed analyses of the nmr spectra of some of these substances were facilitated by heteronuclear double resonance experiments. The vicinal ^1H–^1H and ^{19}F–^1H couplings indicate that while some derivatives have a most marked conformational preference, others have several different conformations significantly populated.

It has been realized for many years that the five-membered rings of metal chelate complexes have the ligand in the gauche conformation.[3] The importance of nonbonded interactions in determining the favored conformations of such derivatives was first pointed out by Mathieu[4] and by Corey and Bailar,[5] and predic-

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(1) Preliminary communication: W. R. Cullen, L. D. Hall, and J. E. H. Ward, *Chem. Commun.*, 625 (1970).

(2) (a) This work is part of the material submitted by J. E. H. W. in partial fulfillment of the requirements for the Ph.D. degree in chemistry, University of British Columbia. (b) This paper may be regarded as part V of a series entitled, "The Conformations of Cyclic Compounds in Solution;" for part IV, see L. D. Hall and R. N. Johnson, to be published.

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