Synthesis, Crystal Structure, and Spectroscopic Properties of $[Mo_2(O_2CMe)_2(MeCN)_6][BF_4]_2$, $[Rh_2(O_2CMe)_2(MeCN)_6][BF_4]_2$, and $[Rh_2(O_2CMe)_2(MeCN)_4(py)_2][BF_4]_2$†

Gillian Pimblett and C. David Garner*
The Chemistry Department, Manchester University, Manchester M13 9PL
William Clegg*
Department of Inorganic Chemistry, The University, Newcastle upon Tyne NE1 7RU

Treatment of $[M_2(O_2CMe)_4]$ (M = Mo or Rh) with $[OMe_3][BF_4]$ (*ca.* 1:4 mol ratio) in MeCN produces the corresponding $[M_2(O_2CMe)_2(MeCN)_6][BF_4]_2$ compound; dissolution of the rhodium derivative in pyridine (py) produces $[Rh_2(O_2CMe)_2(MeCN)_4(py)_2][BF_4]_2$. The structure of each of these compounds has been confirmed by *X*-ray crystallography: $[Mo_2(O_2CMe)_2(MeCN)_6][BF_4]_2$ crystallises in the monoclinic space group $P2_1/m$, with a = 7.160(1), b = 10.642(1), c = 19.402(2) Å, β = 99.47(1)°, and Z = 2; $[Rh_2(O_2CMe)_2(MeCN)_6][BF_4]_2$ crystallises in the monoclinic space group $C2/c$, with a = 15.749(2), b = 18.417(3), c = 13.965(2) Å, β = 91.34(2)°, and Z = 4; $[Rh_2(O_2CMe)_2(MeCN)_4(py)_2][BF_4]_2$ crystallises in the monoclinic space group $C2/m$, with a = 19.448(3), b = 10.476(1), c = 18.990(3) Å, β = 113.25(1)°, and Z = 4. The final R factors (and observed reflections) for the refined structures were 0.053 (2 774), 0.040 (2 936), and 0.059 (2 391), respectively. In each compound, the cation involves a *cis* arrangement of the two μ-acetato-groups, four equatorial *N*-bonded MeCN molecules, and two axial ligands (MeCN or pyridine) co-ordinated to the dimetal(II) centre. For each of the cations, the bond lengths are normal for such species and comparisons within and between values for the $[M_2(O_2CR)_2(MeCN)_6]^{2+}$ (M = Mo or Rh) provide a clear indication of the static *trans* effect of a Mo$\equiv$Mo quadruple bond and a Rh–Rh single bond, together with a clear documentation of the structural similarities and differences for analogous Mo_2^{4+} and Rh_2^{4+} complexes: Mo–Mo 2.136(1), Mo–O_{eq} 2.084(13), Mo–N_{eq} 2.148(4), Mo–N_{ax} 2.759(19); Rh–Rh 2.534(1), Rh–O_{eq} 2.015(4), Rh–N_{eq} 1.983(4), and Rh–N_{ax} 2.232(4) Å. The dimensions of the $Rh_2O_4N_6$ cores of $[Rh_2(O_2CMe)_2(MeCN)_4L_2]^{2+}$ (L = MeCN or py) are virtually identical; the latter complex involves an orthogonal arrangement of the two pyridine rings. Proton and ^{13}C n.m.r. studies have shown that, at ambient temperatures, both the axial and equatorial MeCN molecules of $[Mo_2(O_2CMe)_2(MeCN)_6]^{2+}$ undergo rapid exchange with CD_3CN, whereas for the corresponding rhodium complex only the axial molecules undergo such exchange. U.v.–visible and i.r. data are also reported.

Recently, Telser and Drago[1] reported details concerning the products of the reactions of $[M_2(O_2CR)_4]$ (M = Mo, R = Me; M = Rh, R = Bu^n) in MeCN solution with a strong acid (CF_3SO_3H or $HBF_4{\cdot}Et_2O$). Baranovskii *et al.*[2] have also investigated the reaction of $[Rh_2(O_2CMe)_4]$ with CF_3SO_3H. Such studies represent interesting manifestations of the versatile chemistry possible[3] for a dimetal centre. Telser and Drago demonstrated that these reactions lead to the formation of the corresponding $[M_2(O_2CR)_2]^{2+}$ centres and several such derivatives were characterised by spectroscopy and elemental analyses. These results have prompted us to report synthetic, structural, and spectroscopic information concerning the isolation and characterisation of $[Mo_2(O_2CMe)_2(MeCN)_6][BF_4]_2$,‡ $[Rh_2(O_2CMe)_2(MeCN)_6][BF_4]_2$, and $[Rh_2(O_2CMe)_2(MeCN)_4(py)_2][BF_4]_2$ (py = pyridine) and some related compounds.

Experimental

Trimethyloxonium tetrafluoroborate, $[OMe_3][BF_4]$ (Fluorochem. Ltd.), was used as received. The compounds $[Mo_2(O_2CMe)_4]$, $[Mo_2(O_2CH)_4]$, and $[Rh_2(O_2CMe)_4]$ were prepared as described previously.[4,5] Solvents were dried and purified by distillation under an atmosphere of dinitrogen prior to use. All manipulations were carried out using Schlenk-tube techniques under an atmosphere of dinitrogen. Analyses were performed by Mr. M. Hart and staff in the Microanalytical Laboratory, University of Manchester. Proton n.m.r. spectra were recorded at 220 and and at 300 MHz using Perkin-Elmer R34 and Varian SC300 Fourier-transform spectrometers, respectively, ^{13}C n.m.r. spectra at 20.1 MHz on a Bruker WP-80 Fourier-transform spectrometer. The chemical shifts are reported in p.p.m. relative to $SiMe_4$. Unless stated otherwise, n.m.r. spectra were recorded at ambient temperatures. I.r. and u.v.–visible

---

† Di-μ-acetato-bis[triacetonitrilemolybdenum(II)] (4*Mo–Mo*) and -bis[triacetonitrilerhodium(II)] (*Rh–Rh*) tetrafluoroborate, and di-μ-acetato-bis[diacetonitrilepyridinerhodium(II)] (*Rh–Rh*) tetrafluoroborate.

Supplementary data available (No. SUP 56487, 5 pp.): thermal parameters. See Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1986, Issue 1, pp. xvii—xx. Structure factors are available from the editorial office.

‡ *Note added in proof*: Since the submission of this paper, a note describing the preparation and crystal structure of two compounds containing $[Mo_2(O_2CMe)_2(MeCN)_4L_2]^{2+}$ cations (L = axial ligand) has been published (F. A. Cotton, A. H. Reid, jun., and W. Schwotzer, *Inorg. Chem.*, 1985, **24**, 3965). This includes a rather less precise determination of the structure of $[Mo_2(O_2CMe)_2(MeCN)_6][BF_4]_2$, based on about half the number of data used in the present study.

Table 1. Crystal data and structure determination

	$[Mo_2(O_2CMe)_2(MeCN)_6][BF_4]_2$	$[Rh_2(O_2CMe)_2(MeCN)_6][BF_4]_2\cdot 4MeCN$	$[Rh_2(O_2CMe)_2(MeCN)_4(py)_2][BF_4]_2$
Formula	$C_{16}H_{24}B_2F_8Mo_2N_6O_4$	$C_{24}H_{36}B_2F_8N_{10}O_4Rh_2$	$C_{22}H_{28}B_2F_8N_6O_4Rh_2$
M	729.9	908.0	819.9
Space group	$P2_1/m$	$C2/c$	$C2/m$
a/Å	7.160(1)	15.749(2)	19.448(3)
b/Å	10.642(1)	18.417(3)	10.476(1)
c/Å	19.402(2)	13.965(2)	18.990(3)
β/°	99.47(1)	91.34(2)	113.25(1)
U/Å^3	1 458.2	4 049.4	3 554.8
Z	2	4	4
D_c/g cm^{-3}	1.662	1.489	1.532
$F(000)$	720	1 816	1 624
μ(Mo-K_α)/mm^{-1}	0.919	0.876	0.987
Crystal size/mm	0.2 × 0.2 × 0.4	0.4 × 0.4 × 0.75	0.25 × 0.3 × 0.75
$2\theta_{max.}$/°	55	50	50
Reflections measured	3 753	6 549	6 617
Unique reflections	3 522	3 560	2 391
Observed [$F > 4\sigma(F)$]	2 774	2 936	2 391
R_{int}	0.042	0.038	0.028
Weighting factor g	0.000 68	0.001 25	0.001 00
Number of parameters	214	272	239
R	0.053	0.040	0.059
$R' = (\Sigma w\Delta^2/\Sigma wF_o^2)^{\frac{1}{2}}$	0.069	0.057	0.076
Slope of normal probability plot	1.46	1.03	1.36
Max. peak in final difference map (e Å^{-3})	0.73	0.45	0.88

spectra were recorded on a Pye-Unicam SP3-200 and a Perkin-Elmer 402 spectrometer, respectively.

Di-μ-acetato-bis[triacetonitrilemolybdenum(II)] *Tetrafluoroborate,* $[Mo_2(O_2CMe)_2(MeCN)_6][BF_4]_2$.—The compound $[Mo_2(O_2CMe)_4]$ (1.12 g, 2.62 mmol) was added to a stirred solution of $[OMe_3][BF_4]$ (1.55 g, 10 mmol) in MeCN (50 cm^3). The resultant mixture was maintained at ambient temperature and stirred for *ca.* 30 min, after which time all of the yellow precipitate had reacted to form a clear red solution. Evaporation of solvent under reduced pressure until precipitation commenced, gentle warming, and slow cooling produced a mass of red crystals. The product was separated by filtration and further purified by recrystallisation from MeCN. Yield *ca.* 1.5 g (84%) (Found: C, 26.3; H, 3.3; Mo, 25.7; N, 10.9. Calc. for $C_{16}H_{24}B_2F_8Mo_2N_6O_4$: C, 26.3; H, 3.3; Mo, 26.3; N, 11.5%).

Di-μ-formato-bis[diacetonitrilemolybdenum(II)] *Tetrafluoroborate,* $[Mo_2(O_2CH)_2(MeCN)_4][BF_4]_2$.—This compound was prepared in a manner analogous to that described above for its acetato-analogue, in a powdered or microcrystalline form. Yield *ca.* 80% starting from $[Mo_2(O_2CH)_4]$ (0.6 g, 1.6 mmol) (Found: C, 21.1; H, 2.3; N, 9.7. Calc. for $C_{10}H_{14}B_2F_8Mo_2N_4O_4$: C, 19.4; H, 2.3; N, 9.0%).

Di-μ-acetato-bis[triacetonitrilerhodium(II)] *Tetrafluoroborate,* $[Rh_2(O_2CMe)_2(MeCN)_6][BF_4]_2$.—A solution of $[OMe_3][BF_4]$ (1.17 g, 7.9 mmol) in MeCN (20 cm^3) was added to a suspension of $[Rh_2(O_2CMe)_4(MeOH)_2]$ (1 g, 2 mmol) in MeCN (20 cm^3). This mixture was stirred for *ca.* 8 h, whence a deep purple solution formed. On addition of diethyl ether (20 cm^3), a purple powder precipitated. This solid was collected by filtration and recrystallised from MeCN to afford *ca.* 1.11 g (75% yield) of a crystalline product [Found (for the powdered material): C, 25.7; H, 3.2; F, 20.1; N, 11.3; Rh, 28.2. Calc. for $C_{16}H_{24}B_2F_8N_6O_4Rh_2$: C, 25.8; H, 3.2; F, 20.4; N, 11.3; Rh, 27.7%]. *X*-Ray crystallography showed that the crystalline material has the composition $[Rh_2(O_2CMe)_2(MeCN)_6][BF_4]_2\cdot 4MeCN$.

The corresponding Bu^{t}CN compound, $[Rh_2(O_2CMe)_2(Bu^tCN)_6][BF_4]_2$, was prepared in an analogous manner in Bu^{t}CN (Found: C, 41.4; H, 6.2; F, 14.4; N, 8.3; Rh, 20.3. Calc. for $C_{34}H_{60}B_2F_8N_6O_4Rh_2$: C, 41.0; H, 6.1; F, 15.2; N, 8.4; Rh, 20.6%).

Di-μ-acetato-bis[diacetonitrilepyridinerhodium(II)] *Tetrafluoroborate,* $[Rh_2(O_2CMe)_2(MeCN)_4(py)_2][BF_4]_2$.—The salt $[Rh_2(O_2CMe)_2(MeCN)_6][BF_4]_2$ (0.19 g, 0.25 mmol), prepared as described above, was dissolved in pyridine (20 cm^3) to give an orange solution. Reduction of the volume of this solution by evaporation under reduced pressure, and the addition of diethyl ether (5 cm^3), precipitated an orange powder. This material was collected by filtration and recrystallised from MeOH to yield *ca.* 0.18 g (85% yield) of a crystalline product (Found: C, 32.2; H, 3.5; F, 17.5; N, 10.2; Rh, 24.6. Calc. for $C_{22}H_{28}B_2F_8N_6O_4Rh_2$: C, 32.2; H, 3.4; F, 18.5; N, 10.2; Rh, 25.1%).

X-Ray Crystallography.—Single crystals of $[Mo_2(O_2CMe)_2(MeCN)_6][BF_4]_2$, $[Rh_2(O_2CMe)_2(MeCN)_6][BF_4]_2\cdot 4MeCN$, and $[Rh_2(O_2CMe)_2(MeCN)_4(py)_2][BF_4]_2$, coloured deep red, magenta, and yellow-orange, respectively, prepared as described above and individually sealed in a Lindemann glass capillary, proved suitable for an *X*-ray crystal structure determination. In each case data were collected on a Stoe–Siemens AED diffractometer using graphite-monochromated Mo-K_α radiation (λ = 0.710 69 Å) with a ω—θ scan mode with on-line profile fitting[6] at T = 291 K; no significant variation in standard reflection intensities was observed (except for the molybdenum complex where a steady decay, leading to a reduction of *ca.* 18% in intensity, was corrected for in the data reduction); an absorption or extinction correction was applied; D_m was not measured. Each structure was solved by Patterson and Fourier techniques, including difference syntheses. Blocked-cascade

Table 2. Atomic co-ordinates (× 10^4)

Atom	*x*	*y*	*z*	Atom	*x*	*y*	*z*
(*a*) For $[Mo_2(O_2CMe)_2(MeCN)_6][BF_4]_2$							
Mo(1)	466(1)	2 500	2 256(1)	N(5)	4 564(12)	2 500	484(5)
Mo(2)	2 411(1)	2 500	1 531(1)	C(51)	5 509(16)	2 500	60(6)
O(11)	−1 136(5)	1 102(4)	1 693(2)	C(52)	6 695(24)	2 500	−454(9)
O(12)	844(5)	1 110(4)	928(2)	B(6)	8 471(16)	2 500	7 788(6)
C(11)	−620(7)	682(5)	1 142(3)	F(61)	10 124(15)	2 500	7 692(10)
C(12)	−1 776(10)	−360(7)	748(3)	F(62)	7 233(19)	2 500	7 204(5)
N(2)	1 575(6)	1 102(4)	3 012(2)	F(63)	8 102(12)	1 457(7)	8 096(4)
C(21)	1 935(8)	398(6)	3 453(3)	B(7)	2 439(21)	2 500	5 369(8)
C(22)	2 321(14)	−524(7)	4 025(4)	F(71)	2 127(29)	2 500	4 668(7)
N(3)	4 353(6)	1 079(4)	1 991(2)	F(72)	2 479(31)	1 252(16)	5 620(8)
C(31)	5 332(7)	325(5)	2 264(3)	F(73)	1 128(30)	2 500	5 716(15)
C(32)	6 567(9)	−647(6)	2 615(4)	F(74)	862(32)	2 500	5 039(17)
N(4)	−2 168(12)	2 500	3 155(4)	F(75)	3 633(63)	2 500	5 873(17)
C(41)	−2 610(15)	2 500	3 675(5)	F(76)	3 802(37)	1 878(39)	5 299(23)
C(42)	−3 224(32)	2 500	4 332(7)				
(*b*) For $[Rh_2(O_2CMe)_2(MeCN)_6][BF_4]_2\cdot 4MeCN$							
Rh	4 628(1)	2 934(1)	1 685(1)	C(52)	4 313(4)	792(4)	446(6)
O(11)	5 480(2)	2 168(1)	1 328(2)	N(6)	7 540(4)	3 252(5)	966(5)
O(12)	6 115(2)	2 152(1)	2 776(2)	C(61)	8 169(4)	2 957(4)	979(5)
C(11)	6 024(3)	1 930(2)	1 938(3)	C(62)	8 953(4)	2 583(5)	945(5)
C(12)	6 599(3)	1 323(3)	1 609(4)	B(7)	0	853(7)	2 500
N(2)	5 330(2)	3 696(2)	1 085(2)	F(71)	12(19)	1 454(7)	2 866(15)
C(21)	5 692(3)	4 125(3)	681(3)	F(72)	249(15)	909(17)	1 619(11)
C(22)	6 159(4)	4 676(4)	147(5)	F(73)	−846(10)	936(12)	2 290(18)
N(3)	3 768(2)	3 672(2)	2 011(2)	F(74)	−221(47)	460(27)	1 856(32)
C(31)	3 260(3)	4 090(2)	2 149(3)	F(75)	502(29)	368(20)	2 293(49)
C(32)	2 615(4)	4 641(3)	2 346(5)	B(8)	0	4 315(9)	2 500
N(4)	3 978(2)	2 753(2)	268(3)	F(81)	564(9)	3 811(10)	2 032(14)
C(41)	3 659(3)	2 700(3)	−452(3)	F(82)	−639(6)	4 267(7)	1 677(8)
C(42)	3 267(4)	2 619(5)	−1 408(4)	F(83)	389(8)	4 921(8)	2 309(13)
N(5)	2 678(4)	867(5)	173(8)	F(84)	357(17)	4 257(18)	1 886(20)
C(51)	3 375(5)	810(4)	295(6)				
(*c*) For $[Rh_2(O_2CMe)_2(MeCN)_4(py)_2][BF_4]_2$							
Rh(1)	5 571(1)	5 000	6 887(1)	C(45)	7 881(7)	5 000	6 950(7)
Rh(2)	4 317(1)	5 000	7 018(1)	C(46)	7 247(5)	5 000	7 112(6)
O(11)	5 115(2)	6 363(4)	6 080(2)	N(51)	3 113(5)	5 000	6 856(4)
O(12)	4 022(2)	6 357(4)	6 201(2)	C(52)	2 767(5)	6 215(10)	6 797(4)
C(13)	4 457(4)	6 766(6)	5 922(3)	C(53)	1 979(7)	6 160(17)	6 653(7)
C(14)	4 183(5)	7 826(8)	5 334(4)	C(54)	1 615(14)	5 000	6 614(13)
N(21)	6 057(3)	6 322(5)	7 665(3)	B(1)	4 970(7)	0	2 721(8)
C(22)	6 389(4)	7 031(8)	8 101(4)	F(11)	5 433(17)	792(24)	3 137(13)
C(23)	6 859(6)	8 014(10)	8 673(6)	F(12)	4 755(12)	926(21)	3 007(21)
N(31)	4 557(3)	6 330(6)	7 824(3)	F(13)	4 405(9)	501(13)	2 206(9)
C(32)	4 653(4)	7 061(8)	8 280(4)	F(14)	5 386(11)	−672(18)	2 513(17)
C(33)	4 789(7)	8 027(10)	8 911(5)	B(2)	6 757(8)	0	460(8)
N(41)	6 562(4)	5 000	6 572(4)	F(21)	7 374(8)	0	417(11)
C(42)	6 471(6)	5 000	5 821(6)	F(22)	6 815(8)	0	1 122(6)
C(43)	7 033(5)	5 000	5 582(6)	F(23)	6 390(7)	997(13)	203(8)
C(44)	7 747(8)	5 000	6 142(8)				

least-squares refinement proceeded to a minimum value of $\Sigma w\Delta^2$, where $w^{-1} = \sigma^2(F) + gF^2$ and g was optimised automatically, with anisotropic thermal parameters but without hydrogen atoms. The $[BF_4]^-$ anions were disordered and F-atom positions with partial occupancy factors were refined to account for the observed electron density but no geometrical interpretation was attempted. For the pyridine complex, it was necessary to constrain all B–F distances within the anion to be equal [refined value 1.246(6) Å].

Computer programs were written by W. C. (diffractometer control program) and by Professor G. M. Sheldrick (SHELXTL system).[7] Scattering factors were taken from ref. 8.

A summary of the crystallographic and refinement data is presented in Table 1. Atomic co-ordinates are given in Table 2 and selected bond lengths and angles in Table 3.

Results and Discussion

Crystallographic Studies.—Each of the compounds characterised by *X*-ray crystallography in this study (Figures 1—3) consists of dipositive dimetal cations and (disordered) $[BF_4]^-$ anions; $[Rh_2(O_2CMe)_2(MeCN)_6][BF_4]_2\cdot 4MeCN$ contains extra MeCN molecules in the structure which are readily lost upon drying. Each cation has crystallographic symmetry; $[Mo_2(O_2CMe)_2(MeCN)_6]^{2+}$ and $[Rh_2(O_2CMe)_2(MeCN)_4$-

Table 3. Selected bond lengths (Å) and angles (°)

(*a*) $[Mo_2(O_2CMe)_2(MeCN)_6][BF_4]_2$

Mo(1)–Mo(2)	2.136(1)		
Mo(1)–O(11)	2.075(4)	Mo(2)–O(12)	2.093(4)
Mo(1)–N(2)	2.148(4)	Mo(2)–N(3)	2.147(4)
Mo(1)–N(4)	2.772(8)	Mo(2)–N(5)	2.745(10)
Mo(2)–Mo(1)–O(11)	91.0(1)	Mo(1)–Mo(2)–O(12)	91.1(1)
Mo(2)–Mo(1)–N(2)	104.0(1)	Mo(1)–Mo(2)–N(3)	100.0(1)
Mo(2)–Mo(1)–N(4)	177.9(2)	Mo(1)–Mo(2)–N(5)	173.6(2)
O(11)–Mo(1)–N(2)	88.5(1)	O(12)–Mo(2)–N(3)	89.2(2)
O(11)–Mo(1)–N(4)	87.5(1)	O(12)–Mo(2)–N(5)	84.4(2)
N(2)–Mo(1)–N(4)	77.5(2)	N(3)–Mo(2)–N(5)	84.5(2)
O(11)–Mo(1)–O(11′)	91.5(2)	O(12)–Mo(2)–O(12′)	89.9(2)
N(2)–Mo(1)–O(11′)	165.0(2)	N(3)–Mo(2)–O(12′)	168.8(2)

(*b*) $[Rh_2(O_2CMe)_2(MeCN)_6][BF_4]_2\cdot 4MeCN$

Rh–Rh′	2.534(1)		
Rh–O(11)	2.017(3)	Rh–O(12′)	2.012(3)
Rh–N(2)	1.985(4)	Rh–N(3)	1.980(3)
Rh–N(4)	2.232(4)		
Rh′–Rh–O(11)	85.7(1)	Rh′–Rh–N(2)	97.4(1)
Rh′–Rh–N(3)	95.7(1)	Rh′–Rh–O(12′)	85.7(1)
Rh′–Rh–N(4)	171.4(1)	O(11)–Rh–O(12′)	89.3(1)
O(11)–Rh–N(2)	90.6(1)	O(11)–Rh–N(3)	178.4(1)
O(11)–Rh–N(4)	88.3(1)	O(12′)–Rh–N(2)	176.9(1)
O(12′)–Rh–N(3)	90.0(1)	O(12′)–Rh–N(4)	88.1(1)
N(2)–Rh–N(3)	90.1(1)	N(2)–Rh–N(4)	88.8(1)
N(3)–Rh–N(4)	90.2(1)		

(*c*) $[Rh_2(O_2CMe)_2(MeCN)_4(py)_2][BF_4]_2$

Rh(1)–Rh(2)	2.548(2)		
Rh(1)–O(11)	2.024(4)	Rh(2)–O(12)	2.014(5)
Rh(1)–N(21)	1.973(5)	Rh(2)–N(31)	1.984(6)
Rh(1)–N(41)	2.231(9)	Rh(2)–N(51)	2.238(9)
Rh(2)–Rh(1)–O(11)	85.6(1)	Rh(1)–Rh(2)–O(12)	85.3(2)
Rh(2)–Rh(1)–N(21)	96.9(2)	Rh(1)–Rh(2)–N(31)	97.6(2)
Rh(2)–Rh(1)–N(41)	170.9(2)	Rh(1)–Rh(2)–N(51)	167.6(2)
O(11)–Rh(1)–N(21)	90.5(2)	O(12)–Rh(2)–N(31)	90.4(2)
O(11)–Rh(1)–N(41)	88.0(2)	O(12)–Rh(2)–N(51)	86.0(2)
O(11′)–Rh(1)–N(21)	177.5(3)	O(12′)–Rh(2)–N(31)	177.1(2)
N(21)–Rh(1)–N(41)	89.6(2)	N(31)–Rh(2)–N(51)	91.2(2)
O(11)–Rh(1)–O(11′)	89.7(2)	O(12)–Rh(2)–O(12′)	89.9(3)
N(21)–Rh(1)–N(21′)	89.2(3)	N(31)–Rh(2)–N(31′)	89.2(3)

A prime indicates an atom generated by symmetry (mirror plane or rotation axis).

$(py)_2]^{2+}$ have mirror symmetry and $[Rh_2(O_2CMe)_2(MeCN)_6]^{2+}$ is located on a two-fold axis. Each of of the mutually *cis* acetato-groups spans the dimetal centre, which possesses the normal[3] assembly of one axial and four equatorial ligands per metal with an eclipsed arrangement of the two sets of equatorial donor atoms within each cation. The structures of two other Mo_2^{4+} complexes involving two μ-carboxylato-groups and four monodentate equatorial ligands have been determined: $[Mo_2(O_2CPh)_2Br_2(PBu_3)_2]$[9] and $[Mo_2(O_2CMe)_2Cl_4]^{2-}$,[10] both of which have a *trans* arrangement of bridging ligands. The complexes $[Mo_2\{O_2CCH(NH_3)R\}_2(NCS)_4]\cdot nH_2O$ [R = H (glycine), $n = 1$; R = $CH(CH_3)CH_2CH_3$ (L-isoleucine), $n = 4.5$] have been prepared with the carboxylate groups adopting a *cis* relationship and four monodentate equatorial thiocyanates, in a 'sawhorse' arrangement.[11] The salt $[Rh_2(O_2CMe)_2(py)_6][CF_3SO_3]_2$[2] and the two structures based on the Rh_2^{4+} centre reported herein are the first $[Rh_2(O_2CR)_2L_6]$ (L = a monodentate ligand) complexes to be structurally characterised. Each cation involves a *cis* arrangement of the μ-acetato-groups but the paucity of structural data for complexes of this type means that the factors which determine whether a *cis* or *trans* arrangement of the two μ-carboxylato-groups in $[M_2(O_2CR)_2L_n]$ [$n = 4$ (equatorial ligands) or 6 (four equatorial + 2 axial ligands)] complexes remain to be established.

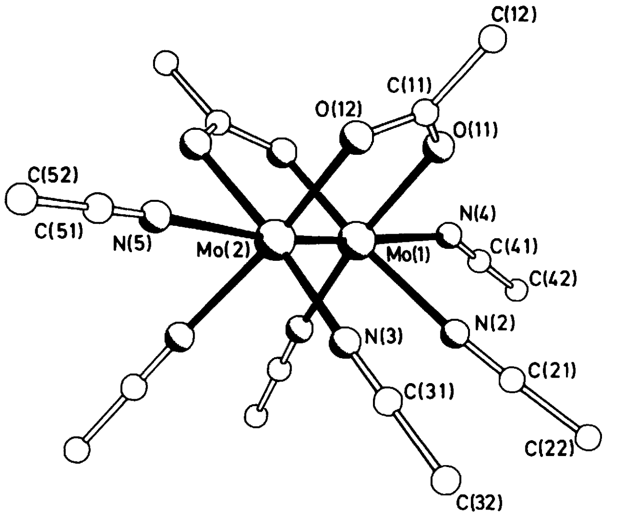

Figure 1. Structure of the $[Mo_2(O_2CMe)_2(MeCN)_6]^{2+}$ cation, showing the labelling of the unique atoms

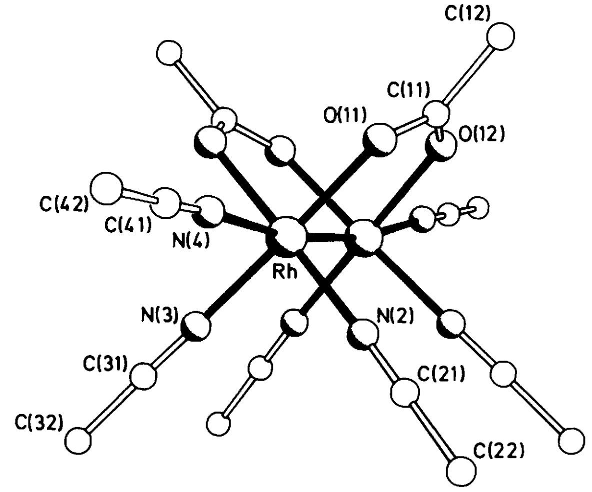

Figure 2. Structure of the $[Rh_2(O_2CMe)_2(MeCN)_6]^{2+}$ cation

With the single exception of Mo(1)–N(4)–C(41), for which the interbond angle is 154.3(8)°, the atoms of the M–N–C–C systems of the co-ordinated acetonitrile groups are essentially linear. The arrangement of the pyridine molecules in $[Rh_2(O_2CMe)_2(MeCN)_4(py)_2]^{2+}$ is interesting, in that the aromatic rings are mutually perpendicular. Therefore, whilst both of the $[M_2(O_2CMe)_2(MeCN)_6]^{2+}$ (M = Mo or Rh) cations approximate to C_{2v} symmetry, the orientation of the planes of the pyridine rings means that $[Rh_2(O_2CMe)_2(MeCN)_4(py)_2]^{2+}$ corresponds to C_s symmetry.

The Mo–Mo distance in $[Mo_2(O_2CMe)_2(MeCN)_6][BF_4]_2$ is typical[2] of complexes containing a quadruple bond between two molybdenum(II) centres; the particular value [2.136(1) Å] may be compared to that in the parent compound $[Mo_2(O_2CMe)_4]$ [2.093 4(8) Å][12] and other structurally character-

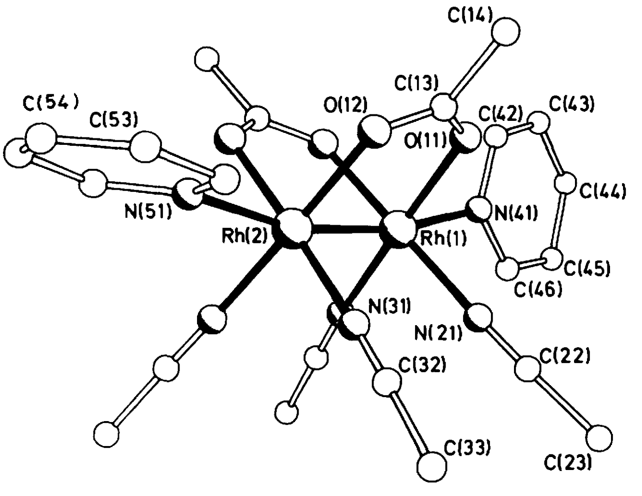

Figure 3. Structure of the $[Rh_2(O_2CMe)_2(MeCN)_4(py)_2]^{2+}$ cation

ised bis(μ-carboxylato)-dimolybdenum(II) complexes, $[Mo_2(O_2CPh)_2Br_2(PBu_3)_2]$ [2.091(3) Å],[9] $[Mo_2(O_2CMe)_2Cl_4]^{2-}$ [2.086(2) Å],[10] $[Mo_2\{O_2CCH_2(NH_3)\}_2(NCS)_4]\cdot H_2O$ [2.132(2) Å] and $[Mo_2\{O_2CCH(NH_3)CH(CH_3)CH_2CH_3\}_2(NCS)_4]\cdot 4.5H_2O$ [2.154(5) Å].[11] The average bond lengths and bond angles of the $Mo(O_2CR)_2Mo$ framework [Mo–O 2.084(13), C–O 1.271(8), and C–C 1.514(9) Å; Mo–Mo–O 91.1(1), O–Mo–O 90.7(1.1), Mo–O–C 118.3(8), and O–C–O 118.3(5)°] are comparable with the corresponding dimensions of $[Mo_2(O_2CMe)_4]$[12] and related structures.[9–13] There is a marked distinction in the length of the Mo–N bonds involving the co-ordinated acetonitrile molecules in the equatorial [2.148(4) Å] as compared to the axial [2.759(19) Å] sites. The former are very similar to the lengths of the $Mo–N_{eq}$ bonds in $[Mo_2\{O_2CCH_2(NH_3)\}_2(NCS)_4]\cdot H_2O$, $[Mo_2\{O_2CCH(NH_3)CH(CH_3)CH_2CH_3\}_2(NCS)_4]\cdot 4.5H_2O$,[11] and $[Mo_2\{BH_3(pz)\}_2(O_2CMe)_2]$[14] (pz = pyrazolyl) of 2.07(2), 2.11(4), and 2.16(2) Å, respectively, whilst the latter may be compared to the $Mo–N_{ax}$ distances in $[Mo_2(O_2CCF_3)_4(py)_2]$ [2.548(8) Å][15] and $[Mo_2\{BH_3(pz)\}_2(O_2CMe)_2]$ [2.45(1) Å].[14] Therefore, the difference between the length of the equatorial and axial Mo–N bonds of $[Mo_2(O_2CMe)_2(MeCN)_6]^{2+}$ has the expected sense ($Mo–N_{ax} > Mo–N_{eq}$) and magnitude (0.61 Å). Furthermore, this complex provides an especially clear and quantitative assessment of the static *trans* effect of a Mo–Mo quadruple bond.

The structural distinction between axial and equatorial MeCN ligands does not extend to their N–C and C–C bond lengths; the overall average lengths of these bonds are 1.13(2) and 1.44(3) Å, respectively, and are normal for MeCN molecules complexed to other metal centres.[16–18] Also, as generally observed[3,9–11] for other complexes of Mo_2^{4+} centres with monodentate ligands, the equatorial MeCN groups make an obtuse angle with the Mo–Mo bond, $Mo–Mo–N_{eq}$ 102(3)°.

A comparison of the relevant bond lengths and angles (Table 3) of $[Mo_2(O_2CMe)_2(MeCN)_6]^{2+}$ and its rhodium analogue provides a clear documentation of the similarities and differences in the detailed structure of Mo_2^{4+} and Rh_2^{4+} complexes and the following observations are made in this respect.

(1) The increase in the length of the metal–metal bond, from 2.136(1) Å in the case of molybdenum to 2.534(1) Å in the case of rhodium, is consistent with a change from a quadruple[2] to a single[19–23] bond. The length of this Rh–Rh bond is within the range 2.359(1)—2.936(2) Å presently considered[19–23] to represent a single bond between two rhodium(II) centres and slightly shorter than that [2.639(2) Å] in $[Rh_2(O_2CMe)_2(py)_6][CF_3SO_3]_2$.[2]

(2) Both the Rh–O and Rh–N equatorial bond lengths are shorter than their molybdenum counterparts, consistent with the smaller covalent radius of rhodium as compared to molybdenum.[24] The Rh–O bond length of 2.015(4) Å is similar but slightly shorter than the lengths of the corresponding bonds in $[Rh_2(O_2CMe)_4(H_2O)_2]$,[25] di-μ-acetato-imidazole-bis(6-methylpyridin-2-olato)dirhodium(II)[26] and -bis(dimethylglyoximato)bis(triphenylphosphine)dirhodium(II)[27] [range 2.027(8)—2.094(6) Å]. The $Rh–N_{eq}$ bonds in these last two compounds and in $[Rh_2(O_2CH)_2(phen)_2Cl_2]$[28] (phen = 1,10-phenanthroline) [range 1.952(4)—2.054(9) Å] are very similar to that [1.983(4) Å] observed for $[Rh_2(O_2CMe)_2(MeCN)_6]^{2+}$. It is of interest to note that, in these $[M_2(O_2CMe)_2(MeCN)_6]^{2+}$ cations, the $M–N_{eq}$ bond undergoes a significantly greater reduction in length than the $M–O_{eq}$ bond, on proceeding from M = Mo to M = Rh; the changes are 0.17 and 0.07 Å, respectively. This parallels the situation observed for the corresponding tetrakis(6-methylpyridin-2-olato)dimetal(II) molecules,[22,29,30] where the corresponding changes are 0.12 and 0.07 Å.

(3) The $Rh–N_{ax}$ bond length of 2.232(4) Å is comparable with those observed for other Rh_2^{4+} complexes containing axially bonded MeCN molecules; $[Rh_2(O_2CMe)_4(MeCN)_2]$,[31] acetonitriletetrakis(6-methylpyridin-2-olato)dirhodium(II),[26] and $[Rh_2(O_2CMe)_2(O_2CCPh_3)_2(MeCN)_2]$[32] involve $Rh–N_{ax}$ distances of 2.254(7), 2.152(7), and 2.19(1) Å, respectively. The $Rh–N_{ax}$ bond in $[Rh_2(O_2CMe)_2(MeCN)_6]^{2+}$ is significantly shorter than that of its molybdenum counterpart, consistent with previous observations[3] that the structural *trans* effect of a Rh–Rh single bond is much less than that of a Mo–Mo quadruple bond. These $[M_2(O_2CMe)_2(MeCN)_6]^{2+}$ (M = Mo or Rh) cations are ideal for a quantitative assessment of the *trans* effects of these metal–metal bonds; the difference $(M–N_{ax}) - (M–N_{eq})$ is 0.61 Å for M = Mo and 0.25 Å for M = Rh. For $[Rh_2(O_2CMe)_2(py)_6][CF_3SO_3]_2$ the difference between $Rh–N_{ax}$ and $Rh–N_{eq}$ is 0.19 Å.[2]

(4) As expected, especially because of the increased length of the M–M separation,[33] the value of the interbond angle $M–M–O_{eq}$ is greater for M = Mo [91.1(1)°] than for M = Rh [85.7(1)°]. Also, $M–M–N_{eq}$, at 96.51(1.2)°, is smaller for $[Rh_2(O_2CMe)_2(MeCN)_6]^{2+}$ than for its molybdenum analogue [102(3)°].

All of the above comments concerning the structure of $[Rh_2(O_2CMe)_2(MeCN)_6]^{2+}$ apply to $[Rh_2(O_2CMe)_2(MeCN)_4(py)_2]^{2+}$, *i.e.* an inspection of Table 3 reveals that corresponding aspects of these two $Rh_2O_4N_6$ cores have virtually identical dimensions. The orthogonal orientation of the two pyridine rings within this latter dirhodium(II) cation could be taken[34] as evidence in favour of significant rhodium–pyridine π-back bonding.[35,36] However, given that the $Rh–N_{py}$ distance in this cation [2.235(5) Å] is not significantly different from that [2.227(2) Å] in $[Rh_2(O_2CMe)_4(py)_2]$,[34] in which the pyridine rings manifest a lack of a preferred orientation with respect to each other, it seems unwise to conclude that the new structural data provide clear evidence for rhodium–pyridine π interactions.

Spectroscopic Studies.—The ^1H n.m.r. spectrum of $[Mo_2(O_2CMe)_2(MeCN)_6][BF_4]_2$ in CD_3CN contains two resonances, at 2.83 and 1.95 p.p.m. with integrations in a *ca.* 1:3 ratio. These values are not in concordance with the ^1H resonances reported by Telser and Drago[1] for $[Mo_2(O_2CMe)_2(MeCN)_4][CF_3SO_3]_2$ and $[Mo_2(O_2CMe)_2(MeCN)_5][BF_3(OH)]_2$; however, these authors were puzzled by their results and suggested that paramagnetic impurities could have caused unusual chemical shifts. Our results appear to be straightforward and we attribute the resonance at 2.83 p.p.m. to the acetate protons, in agreement with the value of 2.63 p.p.m. observed[37] for $[Mo_2(O_2CMe)_4]$ in $(CD_3)_2SO$. The resonance at 1.95 p.p.m. is attributed to MeCN. The relative intensity of these two peaks is consistent with the elemental analytical and crystallographic results for this compound. The observation of a single resonance for the MeCN groups, with this occurring at approximately the position for the solvent, carries the implication that the axial and equatorial MeCN groups are in rapid exchange with each other and with the bulk solvent. The ^{13}C n.m.r. spectrum of $[Mo_2(O_2CMe)_2(MeCN)_6][BF_4]_2$ in CD_3CN is also consistent with this view. Thus, resonances were observed at 1 and 119 p.p.m., corresponding to the methyl and nitrile carbons, respectively, of the solvent. Two other ^{13}C resonances were observed at 25 and 190 p.p.m. and these are assigned to the methyl and carboxylate carbons, respectively, of the acetate groups.

Similar conclusions can be drawn from the ^1H and ^{13}C n.m.r. spectra recorded for $[Mo_2(O_2CH)_2(MeCN)_4][BF_4]_2$, for which satisfactory analytical data proved difficult to obtain; the results implied the easy loss of the two axial MeCN molecules, leaving four MeCN molecules bound to the equatorial sites of the Mo_2^{4+} centre. Thus, in the ^1H n.m.r. spectrum resonances were observed at 1.96 and 9.38 p.p.m.; the former is assigned to the methyl groups of the labile MeCN molecules and the latter {*cf.* $[Mo_2(O_2CH)_4]$ in $(CD_3)_2SO$, 9.20 p.p.m.[37]} to the formate protons. The ^{13}C n.m.r. spectrum in CD_3CN shows resonances at 1 and 120 p.p.m., attributed to CD_3CN as for $[Mo_2(O_2CMe)_2(MeCN)_6]^{2+}$ above, and a further resonance at 178 p.p.m., assigned to the carboxylate carbon.

The ^1H n.m.r. spectra of $[Mo_2(O_2CH)_2(MeCN)_4][BF_4]_2$ in CD_3CN always contained a resonance at 4.14 p.p.m. which varied in intensity from sample to sample. This resonance is attributed to H_2O and, indeed, the solutions were observed to be very hygroscopic. The relative magnitudes of the integrations for the MeCN and formate proton resonances of these spectra were always greater than the 6:1 expected from the molecular formula and the 9:1 assuming ligation of six acetonitrile molecules. We attribute this to a lower intensity for the formate proton resonance, due to an exchange process between the water and the formate protons, since the addition of D_2O causes a (further) significant reduction in the intensity of the formate ^1H resonance.

A comparison of the ^1H n.m.r. spectra of $[Rh_2(O_2CMe)_2(RCN)_6][BF_4]_2$ in CD_3OD (R = Me or Bu^t), the relative integration of the resonances, and the observations by Boyar and Robinson[38] for $[Rh_2(O_2CMe)_4\{P(OMe)_3\}_n]$ (n = 1 or 2) all lead to an unequivocal assignment of these spectra. Apart from features attributable to H_2O and the partially deuteriated solvent, the spectrum of $[Rh_2(O_2CMe)_2(MeCN)_6][BF_4]_2$ contains resonances at 2.65 (equatorial MeCN), 2.09 ($MeCO_2$), and 2.02 p.p.m. (axial, free MeCN), whilst that of $[Rh_2(O_2CMe)_2(Bu^tCN)_6][BF_4]_2$ contains resonances at 2.19 ($MeCO_2$), 1.59 (equatorial Bu^{t}CN), and 1.41 p.p.m. (axial, free Bu^{t}CN). As observed by Boyar and Robinson[38] for $[Rh_2(O_2CMe)_4\{P(OMe)_3\}_n]$,[38] we favour a rapid exchange of the axial ligands of these Rh_2^{4+} complexes with the solvent, the resonance positions for the protons of the axial ligands being very similar to that of the corresponding RCN molecule in CD_3OD. Furthermore, the u.v.–visible spectrum of $[Rh_2(O_2CMe)_2(MeCN)_6][BF_4]_2$ in CH_3OH (see below) is consistent with the replacement of the axial ligands by solvent. However, and in complete contrast to the corresponding dimolybdenum(II) system, $[Rh_2(O_2CMe)_2(MeCN)_6]^{2+}$ (and its Bu^{t}CN analogue) in CD_3OD at ambient temperatures shows no evidence for the exchange of the equatorial nitrile groups. The protons of the equatorial MeCN groups experience a significant downfield shift upon co-ordination to the Rh_2^{4+} centre, being very similar to the shifts observed for MeCN co-ordinated to monomeric Rh^{III},[39] but significantly greater than that for MeCN co-ordinated to monomeric Rh^{I};[18] for the equatorial Bu^{t}CN groups, as expected, the shift of these proton resonances upon co-ordination to Rh_2^{4+} is much smaller.

Similar comments may be made concerning the ^1H n.m.r. spectra of $[Rh_2(O_2CMe)_2(MeCN)_6][BF_4]_2$ in CD_3CN and $[Rh_2(O_2CMe)_2(MeCN)_4(py)_2][BF_4]_2$ in $(CD_3)_2SO$. The former spectrum contains resonances, the relative integrations of which are compatible with the assignments given in parentheses, at 2.54 (equatorial MeCN), 2.04 ($MeCO_2$), and 1.95 (axial, free MeCN); the latter spectrum manifests two sharp resonances at 2.77 (equatorial MeCN) and 2.07 ($MeCO_2$) and three broader features centred at 7.87 (H^3 of py), 8.29 (H^4 of py), and 8.92 p.p.m. (H^2 of py). The shift of the pyridine proton resonances from those (*ca.* 7.3, 7.7, and 8.6 p.p.m.) of pyridine in $(CD_3)_2SO$ is consistent with the retention of the axial co-ordination by this molecule.

The ^{13}C n.m.r. data recorded for the Rh_2^{4+} complexes are consistent with the interpretations of the corresponding ^1H n.m.r. spectra. For $[Rh_2(O_2CMe)_2(MeCN)_4(py)_2][BF_4]_2$ in $(CD_3)_2SO$ the observed resonance positions (and assignments) are 3($\mathit{C}H_3CN$), 23 ($\mathit{C}H_3CO_2$), 126 and 127 ($CH_3\mathit{C}N$ and C^3 of py), 139 (C^4 of py), 150 (C^2 of py),[40] and 192 p.p.m. ($CH_3\mathit{C}O_2$). Similarly, for $[Rh_2(O_2CMe)_2(MeCN)_6][BF_4]_2$ in CD_3CN, the ^{13}C resonances (and assignments) are 4($\mathit{C}D_3CN$), 23 ($\mathit{C}H_3CO_2$), 118 ($CD_3\mathit{C}N$), 126 (equatorial $CH_3\mathit{C}N$), and 194 p.p.m. ($CH_3\mathit{C}O_2$); the resonances for the axial, free $CH_3\mathit{C}N$ and both types of $\mathit{C}H_3CN$ molecules are considered to be obscured under the corresponding solvent resonance. These carboxylate ^{13}C resonance positions are very similar to those observed[39] for $[Rh_2(O_2CMe)_4\{P(OMe)_3\}_n]$ (n = 1 or 2) and, in contrast to the situation for the ^1H resonances of the equatorial MeCN groups, the position of their ^{13}C nitrile resonance corresponds closely to that (128 p.p.m.) for MeCN co-ordinated to monomeric rhodium in $[Rh(PPh_3)_3(MeCN)][BF_4]$.[18]

No evidence for exchange of the equatorial MeCN groups of $[Rh_2(O_2CMe)_2(MeCN)_6][BF_4]_2$ with those of the bulk solvent was obtained by recording the ^1H and ^{13}C n.m.r. spectra of this compound in CD_3CN at *ca.* 55 °C.

The u.v.–visible absorption spectra of $[Mo_2(O_2CMe)_2(MeCN)_6][BF_4]_2$ and $[Mo_2(O_2CH)_2(MeCN)_4][BF_4]_2$ in MeCN show similar features; the lowest-energy band occurs at $\lambda_{max.}$ (ε/dm^3 mol^{-1} cm^{-1}) of 531 (925) and 526 nm (844), respectively, with a shoulder being evident at 395 (150) or 385 nm (234), respectively. These data are very similar to those reported by Telser and Drago[1] for the complexes they formulated as $[Mo_2(O_2CMe)_2(MeCN)_n]^{2+}$ (n = 4 or 5) and are consistent with the spectra of similar complexes[2] involving the Mo_2^{4+} centre and, therefore, the lowest-energy band is assigned to the metal–metal $\delta\rightarrow\delta^*$ promotion.

The electronic spectrum of $[Rh_2(O_2CMe)_2(MeCN)_6][BF_4]_2$ in MeCN shows absorptions with $\lambda_{max.}$ at 520 (202) and 355 nm (478), similar to the electronic spectra of other dirhodium(II) carboxylates,[19,20,41–44] the lowest-energy band having been assigned to the Rh–Rh $\pi^*\rightarrow\sigma^*$ transition[19] or to $\pi^*,\delta^*(Rh_2)\rightarrow\sigma^*(Rh{-}O)$.[44] As seen in the preparation of the bis(pyridine) adduct, the electronic spectrum of which has $\lambda_{max.}$ at 475 (264) and 352 nm (1 547), variation of the axial ligand for Rh_2^{4+} complexes produces a colour change. This is suggested to occur when $[Rh_2(O_2CMe)_2(MeCN)_6][BF_4]_2$ is dissolved in water, MeOH, or tetrahydrofuran; thus a blue solution is formed and the lowest-energy transition occurs at 580, 585, or 596 nm, respectively.

The i.r. spectrum of a Nujol mull of $[Mo_2(O_2CMe)_2(MeCN)_6][BF_4]_2$ contains three sharp bands at 2 340, 2 305, and 2 275 cm^{-1} and that of its rhodium analogue shows a similar profile with absorptions at 2 320, 2 295, and 2 270 cm^{-1};

$[Rh_2(O_2CMe)_2(MeCN)_4(py)_2][BF_4]_2$ shows a single band in this region at 2 295 cm^{-1}. As Telser and Drago[1] suggested, and confirmed by the crystallographic results presented herein, these bands correspond to $\nu(C\equiv N)$ modes of the end-on nitrile groups but, presumably because of lack of resolution and/or weak absorptions, fewer discrete bands are observed than expected given the site symmetry of the cation. However, the details of the $\nu(C\equiv N)$ profile we observed for $[Mo_2(O_2CMe)_2(MeCN)_6][BF_4]_2$ do not agree with those reported by Telser and Drago[1] for related materials.

The other prominent absorptions in the i.r. spectra of these complexes correspond[45] to the $\nu(CO_2)$, $\nu(B-F)$, and (where appropriate) $\nu(C-C)$ and $\nu(C-N)$ modes of the carboxylate, tetrafluoroborate, and pyridine groups, respectively.

Acknowledgements

We thank the S.E.R.C. for the award of a studentship (to G. P.).

References

1 J. Telser and R. S. Drago, *Inorg. Chem.*, 1984, **23**, 1798.
2 I. B. Baranovskii, M. A. Golubnichaya, L. M. Dikareva, and R. N. Shchelokov, *Russ. J. Inorg. Chem.*, 1984, **29**, 872.
3 F. A. Cotton and R. A. Walton, 'Multiple Bonds Between Metal Atoms,' Wiley-Interscience, New York, 1982 and refs. therein; F. A. Cotton, *Acc. Chem. Res.*, 1978, **11**, 225.
4 F. A. Cotton, *Inorg. Synth.*, 1972, **13**, 87.
5 F. A. Cotton, J. G. Norman, jun., B. R. Stults, and T. R. Webb, *J. Coord. Chem.*, 1976, **5**, 217.
6 W. Clegg, *Acta Crystallogr., Sect. A*, 1981, **37**, 22.
7 G. M. Sheldrick, SHELXTL: an integrated system for solving, refining, and displaying crystal structures from diffraction data, University of Göttingen, 1978.
8 'International Tables for *X*-Ray Crystallography,' Kynoch Press, Birmingham, 1974, vol. 4, pp. 99, 149.
9 J. A. Potenza, R. J. Johnson, and J. San Filippo, jun., *Inorg. Chem.*, 1976, **15**, 2215.
10 W. Clegg, C. D. Garner, S. Parkes, and I. B. Walton, *Inorg. Chem.*, 1979, **18**, 2250.
11 A. Bino and F. A. Cotton, *Inorg. Chem.*, 1979, **18**, 1381.
12 F. A. Cotton, Z. C. Mester, and T. R. Webb, *Acta Crystallogr., Sect. B*, 1974, **30**, 2768.
13 F. A. Cotton, M. Extine, and L. D. Gage, *Inorg. Chem.*, 1978, **17**, 172.
14 D. M. Collins, F. A. Cotton, and C. A. Murillo, *Inorg. Chem.*, 1976, **15**, 1861.
15 F. A. Cotton and J. G. Norman, jun., *J. Am. Chem. Soc.*, 1972, **94**, 5697.
16 L. F. Rhodes, J. D. Zubkowski, K. Folting, J. C. Huffman, and K. G. Caulton, *Inorg. Chem.*, 1982, **21**, 4185.
17 F. D. Rochon, R. Melanson, H. E. Howard-Lock, C. J. L. Lock, and G. Turner, *Can. J. Chem.*, 1984, **62**, 860.
18 G. Pimblett, C. D. Garner, and W. Clegg, *J. Chem. Soc., Dalton Trans.*, 1985, 1977.
19 L. Dubicki and R. L. Martin, *Inorg. Chem.*, 1970, **9**, 673.
20 J. G. Norman, jun., and H. J. Kolari, *J. Am. Chem. Soc.*, 1978, **100**, 791.
21 G. G. Christoph and Y. B. Koh, *J. Am. Chem. Soc.*, 1979, **101**, 1422.
22 M. Berry, C. D. Garner, I. H. Hillier, A. A. MacDowell, and W. Clegg, *J. Chem. Soc., Chem. Commun.*, 1980, 494.
23 T. R. Felthouse, *Prog. Inorg. Chem.*, 1982, **29**, 73.
24 L. Pauling, *Proc. Natl. Acad. Sci. USA*, 1975, **72**, 3799.
25 F. A. Cotton, B. G. DeBoer, M. D. LaPrade, J. R. Pipal, and D. A. Ucko, *Acta Crystallogr., Sect. B*, 1971, **27**, 1664.
26 F. A. Cotton and T. R. Felthouse, *Inorg. Chem.*, 1981, **20**, 584.
27 J. Halpern, E. Kimura, J. Molin-Case, and C. S. Wong, *Chem. Commun.*, 1971, 1207.
28 H. Pasternak and F. Pruchnik, *Inorg. Nucl. Chem. Lett.*, 1976, **12**, 591.
29 W. Clegg, C. D. Garner, L. Akhter, and M. H. Al-Samman, *Inorg. Chem.*, 1983, **22**, 2466 and refs. therein.
30 W. Clegg, *Acta Crystallogr., Sect. B*, 1980, **36**, 2437.
31 F. A. Cotton and J. L. Thompson, *Acta Crystallogr., Sect. B*, 1981, **37**, 2235.
32 F. A. Cotton, T. R. Felthouse, and J. L. Thompson, cited in ref. 23.
33 Y. B. Koh and G. G. Christoph, *Inorg. Chem.*, 1979, **18**, 1122.
34 Y. B. Koh and G. G. Christoph, *Inorg. Chem.*, 1978, **17**, 2590.
35 R. S. Drago, S. P. Tanner, R. M. Richman, and J. R. Long, *J. Am. Chem. Soc.*, 1979, **101**, 2897.
36 J. Telser and R. S. Drago, *Inorg. Chem.*, 1984, **23**, 2599 and refs. therein.
37 I. B. Walton, Ph.D. Thesis, University of Manchester, 1979.
38 E. B. Boyar and S. D. Robinson, *J. Chem. Soc., Dalton Trans.*, 1985, 629.
39 B. D. Catsikis and M. L. Good, *Inorg. Chem.*, 1971, **10**, 1522; R. D. Foust and P. C. Ford, *J. Am. Chem. Soc.*, 1972, **94**, 5686.
40 G. C. Levy and G. L. Nelson, 'Carbon-13 Nuclear Magnetic Resonance for Organic Chemists,' Wiley-Interscience, New York, 1972, p. 98.
41 S. A. Johnson, H. R. Hunt, and H. M. Neumann, *Inorg. Chem.*, 1963, **2**, 960.
42 J. G. Norman, jun., G. E. Renzoni, and D. A. Case, *J. Am. Chem. Soc.*, 1979, **101**, 5256.
43 D. S. Martin, jun., T. R. Webb, G. A. Robins, and P. E. Fanwick, *Inorg. Chem.*, 1979, **18**, 475.
44 V. M. Miskowski, W. P. Schaefer, B. Sadeghi, B. D. Santarsiero, and H. B. Gray, *Inorg. Chem.*, 1984, **23**, 1154.
45 K. Nakamoto, 'Infra-red and Raman Spectra of Inorganic and Coordination Compounds,' 3rd edn., Wiley-Interscience, New York, 1977.

Received 12th August 1985; Paper 5/1403