

μ_3 -Oxotrimetal Acetato-complexes of Chromium, Manganese, Iron, Cobalt, Rhodium, and Iridium †

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New pyridine- and β -picoline-containing oxo-centred complex ions $[M_3^{III}O(CO_2Me)_6L_3]^+$, $M = Cr, Mn, Fe, Co, Rh, \text{ and } Ir$, $L = py \text{ and } \beta\text{-pic}$, were synthesised and their redox behaviour studied electrochemically. There is evidence for reduced species in which the oxo-centred triangular structure is maintained in the case of the Mn, Fe, and Co complexes but these could not be isolated. For iridium, complexes $[Ir_3^{III,III,IV}O(CO_2Me)_6L_3]^{2+}$ in which the metal atom is in the mean oxidation state $3\frac{1}{3}$ have also been characterised and shown to undergo reduction to the Ir^{III} species. Attempts to prepare oxo-centred complexes of Cu, Ag, Ni, Pd, Pt, and Mo were unsuccessful. The cobalt complex ion $[Co_3O(CO_2Me)_6L_3]^+$ appears to be different from the other oxo-centred ions and a structure with both bridging and chelate acetato-groups is proposed.

THE green ruthenium(III) complex acetate obtained by interaction of 'ruthenium trichloride trihydrate' with acetic acid and sodium acetate in ethanol has been shown¹ to be of the basic acetate, oxo-centred triangular type previously known for chromium,^{2,3} mangan-

ese,⁴ and iron,^{2,5,6} and to have the formula $[Ru_3O(CO_2Me)_6(H_2O)_3]^+$. Since this ion and also $[Ru_3O(CO_2Me)_6(py)_3]^+$ undergo successive one- and two-electron reductions, and because triphenylphosphine

⁴ L. W. Hessel and C. Romers, *Rec. Trav. chim.*, 1969, **88**, 545.

⁵ A. E. Earnshaw, B. N. Figgis, and J. Lewis, *J. Chem. Soc. (A)*, 1966, 1656.

⁶ K. Anzenhofer and J. J. De Boer, *Rec. Trav. chim.*, 1969, **88**, 286.

† No reprints available.

¹ A. Spencer and G. Wilkinson, *J.C.S. Dalton*, 1972, 1570.

² B. N. Figgis and G. B. Robertson, *Nature*, 1965, **205**, 694.

³ S. C. Chang and G. A. Jeffrey, *Acta Cryst.*, 1970, **B26**, 673.

causes reduction of the aquo-species to $\text{Ru}_3\text{O}(\text{CO}_2\text{Me})_6$ - $(\text{PPh}_3)_3$, which then undergoes a two-electron reduction,¹ it seemed pertinent to check the reducibility of other oxo-centred species. We also attempted to synthesise oxo-centred acetates of other transition metals but with success only for cobalt, rhodium, and iridium.

Synthesis of Oxo-centred Complex Ions.—For the electrochemical studies and in order to eliminate the possibility of ionisation of co-ordinated water, the pyridine

of manganese(II) acetate tetrahydrate with KMnO_4 ,^{4,8} with pyridine or β -picoline and sodium perchlorate in ethanol gave the adducts (E , $L = \text{py}$, $X = \text{ClO}_4$; F , $L = \beta\text{-pic}$, $X = \text{ClO}_4$). Sodium periodate or bismuthate and ozone (in acetic acid) could also be used as oxidants for $\text{Mn}(\text{CO}_2\text{Me})_2 \cdot 4\text{H}_2\text{O}$.

Iron. The cation obtained by interaction of hydrated ferric chloride with sodium acetate in water⁵ or acetic acid⁶ or ethanol-acetic acid on treatment with the

TABLE I
Analytical data and some properties of oxotrimetal acetates

Complex	Analysis Found (Required)				Colour	M.p. (°C)	$\mu_{\text{eff.}}^a$ (B.M.)	M^b Found (Required ^c)
	C	H	N or P	Cl				
<i>A</i> $[\text{Cr}_3\text{O}(\text{CO}_2\text{Me})_6(\text{py})_3]\text{ClO}_4$	37.3(37.6)	3.8(3.9)	4.7(4.9)	4.1(4.1)	Grey	294—295	3.14	450(863)
$[\text{Cr}_3\text{O}(\text{CO}_2\text{Me})_6(\text{py})_3]\text{Cl}$	39.8(40.6)	4.2(4.1)	4.8(5.3)	4.2(4.4)	Grey	> 320		
<i>B</i> $[\text{Cr}_3\text{O}(\text{CO}_2\text{Me})_6(\beta\text{-pic})_3]\text{ClO}_4$	39.7(39.8)	4.3(4.3)	4.0(4.6)	4.1(3.9)	Pale green	> 340	3.28	485(905)
<i>C</i> $[\text{Cr}_3\text{O}(\text{CO}_2\text{Me})_6(\text{MeOH})_3]\text{Cl}$	27.6(27.4)	4.7(4.6)		5.5(5.4)	Green	> 340	3.18	
<i>D</i> $[\text{Cr}_3\text{O}(\text{CO}_2\text{Me})_6(\text{H}_2\text{O})_2(\text{MeCO}_2\text{H})]\text{CO}_2\text{Me}$	27.6(28.2)	4.1(4.3)			Green	> 340		
<i>E</i> $[\text{Mn}_3\text{O}(\text{CO}_2\text{Me})_6(\text{py})_3]\text{ClO}_4$	36.5(37.2)	4.1(3.8)	4.5(4.8)	4.2(4.1)	Brown	218	4.25	440(872)
<i>F</i> $[\text{Mn}_3\text{O}(\text{CO}_2\text{Me})_6(\beta\text{-pic})_3]\text{ClO}_4$	39.4(39.4)	4.1(4.3)	4.4(4.6)	4.0(3.9)	Brown	193—195	4.08	440(914)
<i>G</i> $[\text{Fe}_3\text{O}(\text{CO}_2\text{Me})_6(\text{py})_3]\text{ClO}_4$	36.8(37.1)	3.9(3.8)	4.7(4.8)	4.2(4.1)	Green-yellow	> 340	3.14	455(875)
<i>H</i> $[\text{Fe}_3\text{O}(\text{CO}_2\text{Me})_6(\beta\text{-pic})_3]\text{ClO}_4$	38.4(39.3)	4.2(4.3)	4.4(4.6)	4.2(3.9)	Brown	255—257	3.29	
<i>I</i> $[\text{Co}_3\text{O}(\text{CO}_2\text{Me})_6(\text{py})_3]\text{ClO}_4$	36.6(36.7)	3.7(3.8)	4.6(4.8)	4.1(4.0)	Brown	212	dia.	420(884)
<i>J</i> $[\text{Co}_3\text{O}(\text{CO}_2\text{Me})_6(\beta\text{-pic})_3]\text{ClO}_4$	38.2(38.9)	4.5(4.3)	4.1(4.5)	3.9(3.8)	Yellow-grey	190	dia.	450(926)
<i>K</i> $[\text{Rh}_3\text{O}(\text{CO}_2\text{Me})_6(\text{py})_3]\text{ClO}_4$	31.6(31.9)	3.4(3.3)	4.0(4.1)	3.4(3.5)	Pale yellow	> 320	0.45	
<i>L</i> $[\text{Rh}_3\text{O}(\text{CO}_2\text{Me})_6(\beta\text{-pic})_3]\text{ClO}_4$	34.4(34.1)	4.1(3.7)	3.8(4.0)	3.6(3.4)	Pale yellow	> 320	0.61	
<i>M</i> $[\text{Rh}_3\text{O}(\text{CO}_2\text{Me})_6(\text{H}_2\text{O})_3]\text{ClO}_4 \cdot 2\text{H}_2\text{O}$	17.0(16.6)	3.3(3.3)		4.4(4.1)	Orange-yellow	> 320	0.48	
<i>N</i> $[\text{Rh}_3\text{O}(\text{CO}_2\text{Me})_6(\text{PPh}_3)_3]\text{ClO}_4$	50.8(50.7)	4.2(4.1)	6.0(5.9)	2.5(2.3)	Red-orange	235—238		770(1564)
<i>O</i> $[\text{Ir}_3\text{O}(\text{CO}_2\text{Me})_6(\text{H}_2\text{O})_3]\text{CO}_2\text{Me}$	16.3(15.9)	2.4(2.6)			Green	265—275(d.)		
<i>P</i> $[\text{Ir}_3\text{O}(\text{CO}_2\text{Me})_6(\text{H}_2\text{O})_2(\text{MeCO}_2\text{H})-(\text{CO}_2\text{Me})_2]$	18.1(18.6)	2.4(2.8)			Blue	265—275(d.)	0.96	
<i>Q</i> $[\text{Ir}_3\text{O}(\text{CO}_2\text{Me})_6(\text{H}_2\text{O})_2(\text{MeCO}_2\text{H})]\text{CO}_2\text{Me}$	17.2(17.4)	2.6(2.6)			Pale green	265—275(d.)		
<i>R</i> $[\text{Ir}_3\text{O}(\text{CO}_2\text{Me})_6(\text{py})_3]\text{ClO}_4$	24.4(25.2)	2.6(2.6)	3.2(3.3)	3.1(2.8)	Yellow	> 320	dia.	
<i>S</i> $[\text{Ir}_3\text{O}(\text{CO}_2\text{Me})_6(\beta\text{-pic})_3]\text{ClO}_4$	27.1(27.2)	3.1(3.0)	3.1(3.2)	2.9(2.7)	Yellow	> 320	dia.	
<i>T</i> $[\text{Ir}_3\text{O}(\text{CO}_2\text{Me})_6(\text{py})_3](\text{ClO}_4)_2$	23.4(23.5)	2.5(2.4)	2.9(3.0)	5.1(5.1)	Blue	234		
<i>U</i> $[\text{Ir}_3\text{O}(\text{CO}_2\text{Me})_6(\text{PPh}_3)_3](\text{CO}_2\text{Me})_2$	46.2(45.4)	3.9(3.8)	5.5(5.0)		Light blue	134—135		

^a Per metal ion at 298 K. ^b In CH_2Cl_2 . ^c Neglecting ionisation.

and β -picoline analogues $[\text{M}_3\text{O}(\text{CO}_2\text{Me})_6\text{L}_3]^+$ were prepared. Analytical data and some properties of new compounds are given in Table I.

Chromium. Treatment of hexa-aquochromium(III) chloride with sodium acetate in water or ethanol-acetic acid gave the oxo-centred cation which afforded pyridine, β -picoline, and methanol adducts $[\text{Cr}_3\text{O}(\text{CO}_2\text{Me})_6\text{L}_3]\text{X}$ (A , $L = \text{py}$, $X = \text{ClO}_4$; B , $L = \beta\text{-pic}$, $X = \text{ClO}_4$; C , $L = \text{MeOH}$, $X = \text{Cl}$).⁷ Ozonolysis of chromium(II) acetate dihydrate, $\text{Cr}_2(\text{CO}_2\text{Me})_4(\text{H}_2\text{O})_2$, in acetic acid gave a similar complex D [$L = \text{MeCO}_2\text{H}$, $(\text{H}_2\text{O})_2$, $X = \text{CO}_2\text{Me}$] from which A and B were readily obtained. The known complex with $L = \text{H}_2\text{O}$, $X = \text{Cl}$, obtained from the interaction of chromium(III) hydroxide with hydrochloric and acetic acids,⁵ also gave the same pyridine and β -picoline complexes.

Manganese. Interaction of the known complex $[\text{Mn}_3\text{O}(\text{CO}_2\text{Me})_6(\text{MeCO}_2\text{H})(\text{MeCO}_2)]_n$, from the oxidation

⁷ The pyridine complex of chromium(III) acetate, though of unspecified structure, was obtained by R. F. Weinland and E. Gussmann, *Z. anorg. Chem.*, 1910, **67**, 167; the chloride hydrate was prepared by L. Dubicki and R. L. Martin, *Austral. J. Chem.*, 1969, **22**, 701.

⁸ P. J. Andrusis, jun., M. J. S. Dewar, R. Dietz, and R. L. Hunt, *J. Amer. Chem. Soc.*, 1966, **88**, 5473.

⁹ See S. S. Lande, C. D. Falk, and J. K. Kochi, *J. Inorg. Nuclear Chem.*, 1971, **33**, 4101 and references therein.

amine and sodium perchlorate gave the adducts (G , $L = \text{py}$, $X = \text{ClO}_4$; H , $L = \beta\text{-pic}$, $X = \text{ClO}_4$). These could also be obtained similarly when hydrated iron(II) chloride in acetic acid was ozonised.

Cobalt. The precise nature of the cobalt(III) acetates is uncertain and different synthetic methods give apparently different products.⁹ Oxidation of cobalt(II) acetate has been achieved using oxygen and acetaldehyde,¹⁰ oxygen and butan-2-one,¹¹ peracetic acid,¹² ozone,⁹ and electrochemically.¹³ No X-ray structural study of the products has been made. It has been suggested^{9,12} that the dark green material obtained *via* ozonisation is the dimeric hydroxo-bridged species of the form $\text{Co}_2(\text{CO}_2\text{Me})_4(\text{OH})_2\text{MeCO}_2\text{H}$. Treatment of the green product made by ozonolysis with pyridine and β -picoline in methanol containing sodium perchlorate gave salts, which, according to analyses, have the same stoichiometry as those of Cr^{III} , Mn^{III} , Fe^{III} , Ru^{III} ,

¹⁰ U. Kopsch and W. O. Walker, Canadian Patent 367,728/1937.

¹¹ E. I. Heiba, R. M. Dessau, and W. J. Koehl, jun., *J. Amer. Chem. Soc.*, 1969, **91**, 6830.

¹² E. Koubeck and J. O. Edwards, *J. Inorg. Nuclear Chem.*, 1963, **25**, 1401.

¹³ C. Shall and H. Markgraff, *Trans. Amer. Electrochem. Soc.*, 1924, **45**, 161; C. Shall and C. T. Wiedtmarckter, *Z. Electrochem.*, 1929, **35**, 337; J. Sharp and A. White, *J. Chem. Soc.*, 1952, 110.

Rh^{III}, and Ir^{III} and hence we formulate them as oxo-centred species, $[\text{M}_3\text{O}(\text{CO}_2\text{Me})_6\text{L}_3]\text{ClO}_4$ (I , $L = \text{py}$; J , $L = \beta\text{-pic}$). However, as discussed below, spectroscopic evidence suggests that the structure may not be the same as for the other complexes which are known to be isomorphous.

Rhodium. During our studies it was reported¹⁴ that the interaction of hydrated rhodium(III) chloride and silver acetate in aqueous acetic acid gives the oxo-centred species $[\text{Rh}_3\text{O}(\text{CO}_2\text{Me})_6(\text{H}_2\text{O})_3]\text{X}$. We had prepared the same species by ozonolysis of rhodium(II) acetate in acetic acid and had isolated a number of salts (K , $L = \text{py}$, $X = \text{ClO}_4$; L , $L = \beta\text{-pic}$, $X = \text{ClO}_4$; M , $L = \text{H}_2\text{O}$, $X = \text{ClO}_4, 2\text{H}_2\text{O}$; N , $L = \text{PPh}_3$, $X = \text{ClO}_4$).

Iridium. Treatment of iridium(III) chloride hydrate or 'chloroiridic acid' with silver acetate in acetic acid

derivative $[\text{Ir}_3\text{O}(\text{CO}_2\text{Me})_6(\text{PPh}_3)_3](\text{CO}_2\text{Me})_2$ (U) was obtained from P in methanol at room temperature.

Attempts to prepare oxo-centred complexes of other metals in the III oxidation state by ozonisation of the metal(I) or metal(II) acetates in acetic acid or by oxidation using sodium periodate or bismuthate were unsuccessful for Cu, Ag, Ni, Pd, Pt, and Mo. Attempts to obtain triphenylphosphine derivatives of the Cr, Mn, Fe, and Co complexes also failed.

Electronic, Infrared, and N.M.R. Spectra.—The electronic absorption spectra (Table 2) serve as a guide for characterisation of the species. The spectrum of $[\text{Cr}_3\text{O}(\text{CO}_2\text{Me})_6(\text{H}_2\text{O})_3]\text{Cl}, 6\text{H}_2\text{O}$ has recently been treated theoretically.¹⁵ The spectra of the iridium complexes may be compared with those of the oxo-tri-iridium sulphate $[\text{Ir}_3\text{O}(\text{SO}_4)_6]^{4-}$ recently reported.¹⁶ I.r. spectra

TABLE 2
Electronic absorption spectra of oxoacetato-complexes: $[\text{M}_3\text{O}(\text{CO}_2\text{Me})_6\text{L}_3]\text{X}^a$

Complex	$\lambda_{\text{nm}}(\epsilon)$						
Cr ^b	<i>A</i>	675(40)	560(120)	430(180)	ca. 357sh	ca. 345sh	256(12 300)
	<i>B</i>	675(40)	565(110)	430(170)	ca. 357sh	ca. 345sh	263(13 300)
	<i>C</i>	ca. 670sh	586(110)	441(120)	ca. 355sh	ca. 345sh	ca. 254sh
	<i>D</i>	ca. 670sh	586(130)	441(150)	ca. 357sh	ca. 345sh	ca. 250sh
Mn ^b	<i>E</i>	ca. 550sh	ca. 440sh	ca. 256sh	250(18 800)		
	<i>F</i>	ca. 550sh	441(740)	260(13 000)	255(12 800)		
	<i>c</i>	ca. 550sh	441	240			
Fe ^d	<i>G</i>	ca. 525sh	462(220)	310(7700)	245(19 800)		
	<i>H</i>	ca. 525sh	467(250)	310(8500)	356(20 400)		
	<i>e</i>	ca. 525sh	ca. 467sh	310(9800)	ca. 235sh		
Co ^b	<i>I</i>	ca. 575sh	ca. 340sh	ca. 235sh			
	<i>J</i>	ca. 575sh	ca. 340sh	ca. 235sh			
	<i>f</i>	614	ca. 340sh	ca. 235sh			
Rh ^b	<i>K</i>	312(6200)	250(24 300)				
	<i>L</i>	312(6800)	250(26 400)				
	<i>M</i>	ca. 540sh	357(2900)				
	<i>N</i>	ca. 485sh	350(18 200)	296(42 000)			
Ir ^b	<i>O</i>	ca. 335sh					
	<i>P</i>	1200(2500)	ca. 780sh	660(2800)	ca. 275sh		
	<i>Q</i>	ca. 310sh					
	<i>R</i>	367(7750)	250(21 600)				
	<i>S</i>	367(7350)	258(24 300)				
	<i>T</i>	1120(1400)	685(2500)	367(4800)			
	<i>U</i>	1200(2100)	780(970)	667(2200)	250(44 200)		

^a For spectra of $[\text{M}_3\text{O}(\text{CO}_2\text{Me})_6\text{L}_3]^+$, $M = \text{Cr}$ or Fe , $L = \text{H}_2\text{O}$, py , NH_3 etc. see also L. Dubicki and R. L. Martin, *Austral. J. Chem.*, 1969, **22**, 701. ^b In methanol. ^c Manganese(III) acetate. ^d In ethanol. ^e $[\text{Fe}_3\text{O}(\text{CO}_2\text{Me})_6(\text{H}_2\text{O})_3]\text{Cl}, 3\text{H}_2\text{O}$. ^f Cobalt(III) acetate. ^g Not calculated for the Mn^{III} and Co^{III} acetates since the structures are uncertain.

gave a green oxo-centred iridium(III,II,II) acetate, $[\text{Ir}_3\text{O}(\text{CO}_2\text{Me})_6(\text{H}_2\text{O})_3]\text{CO}_2\text{Me}$ (O). Ozonisation of this in acetic acid afforded the blue(III,III,IV) acetate, $[\text{Ir}_3\text{O}(\text{CO}_2\text{Me})_6(\text{H}_2\text{O})_2(\text{MeCO}_2\text{H})](\text{CO}_2\text{Me})_2$ (P). Electrochemical reduction of a concentrated aqueous solution of P gave the corresponding iridium(III,III,III) species $[\text{Ir}_3\text{O}(\text{CO}_2\text{Me})_6(\text{H}_2\text{O})_2(\text{MeCO}_2\text{H})]\text{CO}_2\text{Me}$ (Q). The amine derivatives $[\text{Ir}_3\text{O}(\text{CO}_2\text{Me})_6\text{L}_3]\text{ClO}_4$ (R , $L = \text{py}$; S , $L = \beta\text{-pic}$), were obtained either from O , P , or Q in boiling ethanol. The formation of R and S from P involves a one-electron reduction evidently by ethanol. The pyridine adduct of the iridium(III,III,IV) species was obtained as a perchlorate salt, $[\text{Ir}_3\text{O}(\text{CO}_2\text{Me})_6\text{py}_3](\text{ClO}_4)_2$ (T), by electrochemical oxidation of a concentrated methanolic solution of R . The triphenylphosphine

(KBr disc) of the pyridine and β -picoline perchlorates $[\text{M}_3\text{O}(\text{CO}_2\text{Me})_6\text{L}_3]\text{ClO}_4$ showed the expected bands for ClO_4^- (1090 cm^{-1}) and bridging acetate, the carboxylate frequencies, ν_{asym} and ν_{sym} being: Cr, 1620, 1450; Mn, 1610, 1395; Fe, 1590, 1440; Rh, 1616, 1425; Ir, 1610, 1425 cm^{-1} . The n.m.r. spectra of the rhodium and iridium complexes (in CDCl_3) showed the expected singlet methyl resonances of acetate (K , τ 7.74; L , τ 7.70; N , τ 8.38; R and S , τ 7.60).

The cobalt(III) complexes appear not to have the same structure as the other species, despite the apparently similar stoichiometry. Thus the i.r. spectra of the pyridine and β -picoline salts have shoulders on the carboxylate frequencies (1590, 1565sh; 1450sh, 1415

¹⁵ L. Dubicki and P. Day, *Inorg. Chem.*, 1972, **11**, 1868.

¹⁶ D. B. Brown, M. B. Robin, J. D. E. McIntyre, and W. F. Peck, *Inorg. Chem.*, 1970, **9**, 2315.

¹⁴ I. B. Baranovskii, G. Ya. Mazo, and L. M. Dikareva, *Russ. J. Inorg. Chem.*, 1971, **16**, 1388.

cm^{-1}). The n.m.r. spectrum of the β -picoline complex perchlorate (the solubility of the pyridine perchlorate is too low for measurement) has the methyl resonances of acetate at τ 8.0 and 7.78 in the ratio 1 : 1 (the methyl of β -picoline is at τ 7.4). The n.m.r. spectrum of crude $[\text{Co}_3\text{O}(\text{CO}_2\text{Me})_6\text{py}_3]\text{Cl}$ also has two methyl singlets at τ 8.6 and 8.2. Finally, while X-ray powder patterns of the pyridine perchlorates of Cr, Mn, Fe, Ru, Rh, and Ir show that they are isomorphous, there are some additional lines in the pattern of the cobalt salt (Table 3).

TABLE 3
X-Ray powder diffraction data for the complexes
 $[\text{M}_3\text{O}(\text{CO}_2\text{Me})_6\text{py}_3]\text{ClO}_4$

Co		Cr, Mn, Fe, Ru, Rh, Ir	
I	d_α	I	d_α
10	14.24	30	10.49
40	10.49	15	8.81
25	8.31		
30	7.61	30	7.61
10	7.38		
		10	7.16
20	7.07		
20 ^a	6.77	20	6.50
		100	4.15
100 ^b	4.15	5	3.94
10	3.85		
60 ^b	3.74	60	3.74
10	2.99	10	2.99
20	2.489	20	2.489
15	2.230	15	2.230
5	2.071	5	2.071
5	1.869	5	1.869

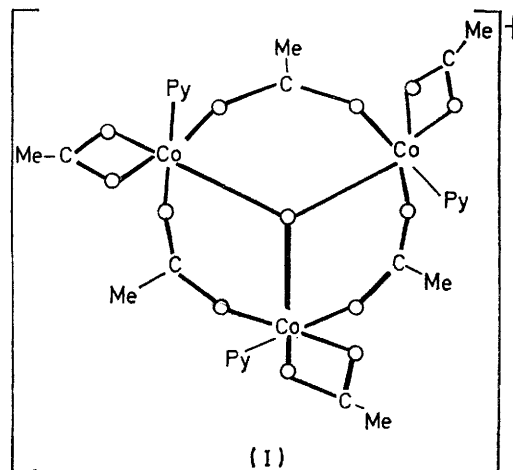
^a Very broad. ^b Line due to Vaseline.

Our conclusion is that there are two types of acetate group probably one bridging and one chelating. It may be noted that recent X-ray study¹⁷ of trisdimethoxyethane-tri- μ -trifluoroacetato- μ_3 -chloro- μ_3 -sulphato-tri-cobalt(II) shows the presence of a bridged trifluoroacetato group between two cobalt atoms and a chelating dimethoxyethane. A structure of the cobalt(II) oxo-acetato cation which would accommodate the stoichiometry and spectra is shown in (I) in which each Co^{III} atom is octahedral with a chelating acetate and a pyridine ligand and each pair of cobalt atoms is bridged by a single acetate group. The ions are diamagnetic as expected for cobalt(III).

We have been unable, by adding perchlorate ion to solutions of the green material produced by ozonisation and studied by Kochi *et al.*,⁹ to obtain corresponding salts with water or acetic acid in place of the amine. The solubility of these green materials in organic solvents, their paramagnetism, and the presence of hydroxo bands in the i.r. spectra indicate that their structure is not an oxo-centred one, but we can add nothing to suggestions already discussed.⁹ The complex ions we have obtained appear to be formed from the green material essentially quantitatively; the presence of the amine may well be the determining factor.

A possible explanation for the different behaviour of

Co^{III} compared to the other M^{III} ions is that it has the smallest ionic radius.



Attempts to Reduce μ_3 -Oxotrimetal Cations.—As noted earlier, the $[\text{Ru}_3\text{O}(\text{CO}_2\text{Me})_6\text{L}_3]^+$ species can be reduced. The reduction and oxidation of the above pyridine, β -picoline, and triphenylphosphine complexes was studied electrochemically using either a dropping mercury electrode or a rotating platinum electrode for acetone solutions containing sodium perchlorate as supporting electrolyte.

The chromium complexes showed neither reduction nor oxidation waves in the range $+2.0$ to -1.8 V *vs.* s.c.e.

The manganese (*E*, *F*) and iron (*G*) complexes were irreversibly reduced at *ca.* $+0.3$ and -0.03 V *vs.* s.c.e. respectively. The *n* values obtained from controlled potential reduction using a platinum foil electrode were low ($n = 0.7$ — 0.8) but suggest a one-electron reduction; there was no oxidation wave. Attempts to isolate the reduced species were unsuccessful.

The complex $[\text{Co}_3\text{O}(\text{CO}_2\text{Me})_6(\beta\text{-pic})_3]\text{ClO}_4$ showed an irreversible one-electron reduction wave at $+0.13$ V *vs.* s.c.e. ($n = 1.1$) and the initial brown colour of the solution changed to yellowish green; there was no oxidation wave. Attempts to isolate the reduced species were unsuccessful and the reduced form was not reoxidised to the starting material in air.

The ions $[\text{Rh}_3\text{O}(\text{CO}_2\text{Me})_6\text{L}_3]^+$, $\text{L} = \text{H}_2\text{O}$, py , showed only an irreversible reduction wave at *ca.* -0.9 to -1.0 V *vs.* s.c.e., while controlled potential reduction gave only rhodium metal and the *n* values were irreproducible. A similar situation was observed with the triphenylphosphine complex.

The iridium(III,III,III) complex (*R*) was irreversibly oxidised at $+0.54$ V *vs.* s.c.e. to the (III,III,IV) species (*T*), the initial yellow solution changing to deep blue ($n = 0.98$); there was no reduction wave. The iridium (III,III,IV) complex, *P*, in water showed an irreversible one-electron reduction wave at $+0.53$ V *vs.* s.c.e. ($n = 0.91$) and the initial blue solution changed to pale yellow giving *Q*, while this pale yellow solution turned to

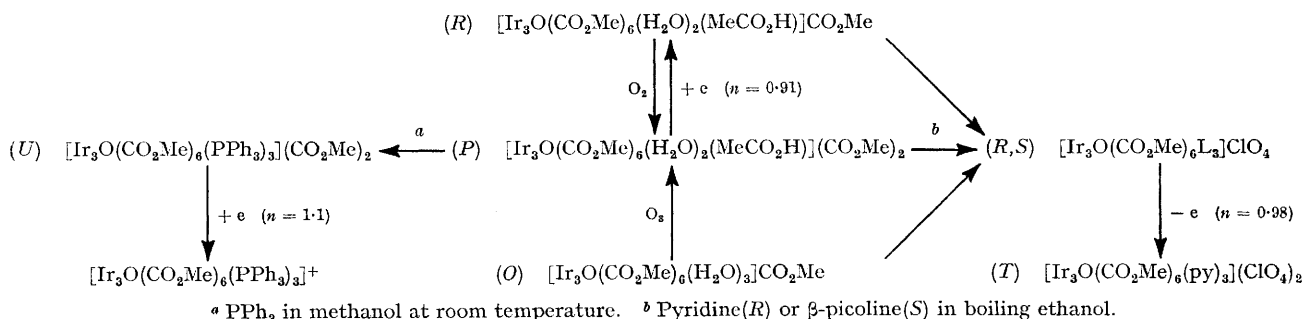
¹⁷ J. Estienne and R. Weiss, *Chem. Comm.*, 1972, 862.

blue on standing in air. The triphenylphosphine complex, *U*, showed an irreversible one-electron reduction wave at -0.17 V vs. s.c.e. ($n = 1.1$) and an irreversible oxidation wave at ca. $+0.1$ V vs. s.c.e., which is probably due to phosphorus. The reactions of the iridium complexes are summarised in the Scheme.

Using hydrogen (2 atmos.) and platinum oxide catalyst¹ or sodium borohydride in ethanol, the aquo pyridine and β -picoline complexes of Mn, Fe, and Co were readily reduced to the simple metal(II) ions. The rhodium complexes were reduced to the metal. The

(II) acetate dihydrate (1 g) was suspended in acetic acid (250 ml) and ozonised at refluxing temperature for 24 h. The dark green solution was filtered and the filtrate was evaporated to dryness to give a green residue (0.6 g). This crude product was dissolved in hot acetic acid and filtered; after cooling to room temperature, ether was added to afford the green complex. This is soluble in water and acetic acid and insoluble in alcohols, ether, acetone, and chloroform.

$[\text{Cr}_3\text{O}(\text{CO}_2\text{Me})_6(\text{py})_3]\text{ClO}_4$ (*A*) and $[\text{Cr}_3\text{O}(\text{CO}_2\text{Me})_6(\text{py})_3]\text{Cl}$.—Freshly prepared chromium(III) hydroxide [from $\text{CrCl}_3 \cdot 6\text{H}_2\text{O}$ (6 g) and aqueous NH_4OH] was dissolved in hydrochloric acid (conc., 10 ml) and acetic acid (40 ml)⁵ and the



SCHEME Reactions of oxotri-iridium acetates

iridium(III,III,IV) complexes were reduced first to the (III,III,III) analogues, and then to iridium(I) species and/or metal. The chromium complexes were unaffected under the same conditions.

The electrochemical reduction of the Mn, Fe, and Co complexes by one electron only suggests that the reduced species retain the trinuclear structure, as in the case of ruthenium.¹ The absence of any evidence for trinuclear species containing the metal ions in oxidation state (II) with rhodium and iridium presumably reflects the relative instability of this oxidation state for those metals compared with those of the first row.

EXPERIMENTAL

Rhodium trichloride hydrate, iridium trichloride hydrate, and chloroiridic acid were from Johnson Matthey Limited. Other reagents were AnalaR grade. Elemental analyses (Table I) were by the Microanalytical Laboratory, Imperial College. N.m.r. spectra were recorded on Perkin-Elmer R12A (60 MHz) and R14 (100 MHz) spectrometers in CDCl_3 using hexamethyldisiloxane as internal reference. I.r. spectra were recorded on a Perkin-Elmer 257 instrument and electronic spectra on a Cary 14 recording spectrophotometer. M.p.s (uncorrected) were measured in unsealed capillary tubes using an Electrothermal apparatus. Electrochemical reduction and oxidation were investigated by using a Beckmann Electroscan TM30 polarograph as previously reported.¹ Molecular weights were obtained on a Hitachi-Perkin-Elmer 115 using CH_2Cl_2 as solvent. Magnetic measurements were made using the Evans' modification of the Gouy balance. Ozone was generated by a Gallenkamp ozoniser. The X-ray powder photographs were recorded on a Nonius Guinier Camera type Y919. Reduction under hydrogen pressure was carried out as previously reported.¹

$[\text{Cr}_3\text{O}(\text{CO}_2\text{Me})_6(\text{H}_2\text{O})_2(\text{MeCO}_2\text{H})]\text{CO}_2\text{Me}$ (*D*).—Chromium-

resulting dark green solution was evaporated to ca. 20 ml. After filtration, the solution was evaporated to dryness to give a green residue (3.5 g). Water (6 ml) and then pyridine (2.6 g) were added and the solution was heated at 60° for 2 min to give the grey pyridine salt $[\text{Cr}_3\text{O}(\text{CO}_2\text{Me})_6(\text{py})_3]\text{Cl}$ (2.5 g). The electronic absorption spectrum of this adduct was the same as that of *A*. Soluble in water and alcohols, slightly soluble in acetone, insoluble in benzene and ether. M.p. $>320^\circ$, slowly decomposed from 220° .

This compound (1.6 g) and $\text{NaClO}_4 \cdot \text{H}_2\text{O}$ (0.28 g) were dissolved in water (50 ml) and the resulting grey perchlorate (*A*, 1.3 g) was filtered off and dried.

$[\text{Cr}_3\text{O}(\text{CO}_2\text{Me})_6(\beta\text{-pic})_3]\text{ClO}_4$ (*B*).—Complex *D* (2 g), β -picoline (0.8 g), and $\text{NaClO}_4 \cdot \text{H}_2\text{O}$ (0.4 g) were dissolved in ethanol (30 ml) and heated at 60° for 5 min to give *B* (0.41 g). A similar treatment using pyridine gave *A*. *A* and *B* are soluble in CH_2Cl_2 , CHCl_3 , acetone, CH_3CN , DMF, DMSO, and pyridine, slightly soluble in alcohols, acetic acid, THF, and insoluble in water, benzene, CCl_4 , ether, and light petroleum.

$[\text{Cr}_3\text{O}(\text{CO}_2\text{Me})_6(\text{MeOH})_3]\text{Cl}$ (*C*).—A mixture of $\text{CrCl}_3 \cdot 6\text{H}_2\text{O}$ (2.7 g, 10 mmol) and $\text{NaCO}_2\text{Me} \cdot 3\text{H}_2\text{O}$ (2.8 g, 20 mmol) was heated at 90° for 4 h in ethanol-acetic acid (1 : 1, 100 ml) solvent. The sodium chloride formed was filtered off and the filtrate was evaporated to dryness. After dissolving the residue in methanol (15 ml), acetone (200 ml) was added and the solution was kept at 10° for 6 h to give green needle crystals of *C* (1.2 g). Soluble in water and alcohols, and insoluble in benzene, CHCl_3 , acetone, and acetic acid.

$[\text{Mn}_3\text{O}(\text{CO}_2\text{Me})_6(\text{py})_3]\text{ClO}_4$ (*E*).—Pyridine (0.5 g) and $\text{NaClO}_4 \cdot \text{H}_2\text{O}$ (0.2 g) were added to an ethanolic solution (10 ml) containing the so-called Mn(III) acetate⁸ (0.30 g) prepared from Mn(II) acetate and KMnO_4 and the solution was heated at 50° for 2 min and allowed to stand for 30 min at room temperature to give the brown precipitate (*E*, 0.27 g), which was purified by washing with a small amount of ethanol and then with ether.

$[\text{Mn}_3\text{O}(\text{CO}_2\text{Me})_6(\beta\text{-pic})_3]\text{ClO}_4$ (*F*).—Similar treatment to the above using Mn(III) acetate (0.5 g) and β -picoline (0.2 g) gave brown needle crystals of *F* (0.3 g). The solubilities of *E* and *F* are similar to those of the chromium analogues.

On ozonisation of Mn^{II} acetate tetrahydrate (2 g) in acetic acid (250 ml) at 100° for 20 min, the colourless solution changed to brown and gave a brown solid (2.3 g) on evaporation of the solvent to dryness. *E* and *F* were obtained by treating this brown solid as above in methanol.

$[\text{Fe}_3\text{O}(\text{CO}_2\text{Me})_6(\text{py})_3]\text{ClO}_4$ (*G*).—To $[\text{Fe}_3\text{O}(\text{CO}_2\text{Me})_6(\text{H}_2\text{O})_3]\text{Cl}\cdot 3\text{H}_2\text{O}$ (0.7 g) prepared according to the literature⁶ were added water (3 ml), pyridine (0.5 g), and $\text{NaClO}_4\cdot\text{H}_2\text{O}$ (0.2 g). The mixture was heated at 60° for 5 min and then kept at 0° for 1 h. The yellowish green solid (0.4 g) was collected by filtration and washed with a small amount of methanol.

$[\text{Fe}_3\text{O}(\text{CO}_2\text{Me})_6(\beta\text{-pic})_3]\text{ClO}_4$ (*H*).— $[\text{Fe}_3\text{O}(\text{CO}_2\text{Me})_6(\text{H}_2\text{O})_3]\text{Cl}\cdot 3\text{H}_2\text{O}$ (0.5 g) was heated with β -picoline (0.2 g) and $\text{NaClO}_4\cdot\text{H}_2\text{O}$ (0.2 g) in ethanol (10 ml) at 60° for 10 min. The precipitated yellowish brown solid *H* (0.3 g) was collected and washed with a slight amount of CH_2Cl_2 . *G* and *H* are soluble in CH_2Cl_2 , CHCl_3 , acetone, CH_3CN , DMF, DMSO, pyridine, and ethanol, slightly soluble in benzene, CCl_4 , acetic acid, water, THF, and insoluble in ether and light petroleum.

On ozonisation of iron(II) chloride (5 g) in acetic acid (250 ml) at room temperature for 5 h, the yellowish brown solution changed to red-brown and gave the orange-brown solid (8.5 g) by evaporation of the solvent to dryness. This solid was recrystallised from acetic acid to give the red-orange solid $[\text{Fe}_3\text{O}(\text{CO}_2\text{Me})_6(\text{H}_2\text{O})_3]\cdot\text{FeCl}_4\cdot 2\text{MeCO}_2\text{H}$.⁶ Soluble in water, alcohols, ether, and CH_2Cl_2 . M.p. 178—182° (d.). *G* and *H* were also obtained by treating this solid as above in ethanol.

$[\text{Co}_3\text{O}(\text{CO}_2\text{Me})_6(\text{py})_3]\text{ClO}_4$ (*I*) and cobalt(III) acetate.—Cobalt(II) acetate tetrahydrate (24.9 g) in acetic acid (250 ml) was ozonised at room temperature for 19 h, the initial colour of the solution changing to dark green. The solvent was evaporated to dryness to give a green residue. This crude acetate was dissolved in chloroform and filtered from the insoluble part, and then light petroleum (60—80°) was added to the filtrate to give the green 'cobalt(III) acetate'. M.p. (d.) 230—233°. Reproducible CH analyses were not obtained from different preparations. The solubility of this substance is the same as that reported.⁹

Pyridine (0.4 g) and $\text{NaClO}_4\cdot\text{H}_2\text{O}$ (0.2 g) were added to a methanolic (10 ml) solution of 'cobalt(III) acetate' (1 g) and the resulting solution was kept at room temperature for 1 h to give the brown perchlorate salt, *I* (0.3 g). More *I* (0.29 g) was obtained from the filtrate after it had stood for another 10 h and this was collected and washed with ether to give pure *I*. Slightly soluble in CH_3CN , DMF, and CH_2Cl_2 and insoluble in CHCl_3 , acetone, pyridine, THF, alcohols, acetic acid, water, ether, CCl_4 , and light petroleum.

$[\text{Co}_3\text{O}(\text{CO}_2\text{Me})_6(\beta\text{-pic})_3]\text{ClO}_4$ (*J*).—A similar procedure using β -picoline gave *J* (0.6 g). Soluble in CH_3CN , DMF, DMSO, pyridine, acetone, CHCl_3 , and CH_2Cl_2 , slightly soluble in alcohols, acetic acid, and THF, and insoluble in ether, benzene, light petroleum, CCl_4 , and water.

$[\text{Rh}_3\text{O}(\text{CO}_2\text{Me})_6(\text{H}_2\text{O})_3]\text{ClO}_4\cdot 2\text{H}_2\text{O}$ (*M*).—The green solution of rhodium(II) acetate, $[\text{Rh}(\text{CO}_2\text{Me})_2]_2$ (0.9 g), in acetic acid (250 ml) was ozonised at refluxing temperature for 2 h to give a clear red-brown solution. Removal of solvent left crude yellow oxorhodium(III) acetate (1.1 g). Water (2 ml) and 60% HClO_4 (0.18 g) were added to this crude acetate (0.8 g) and the mixture was dried over P_2O_5 to give

the perchlorate salt, *M* (0.32 g). The i.r. spectrum and the solubility of *M* were identical to those of a sample prepared by the literature method.¹⁴

$[\text{Rh}_3\text{O}(\text{CO}_2\text{Me})_6(\text{py})_3]\text{ClO}_4$ (*K*).—A mixture of crude oxorhodium(III) acetate (0.4 g), pyridine (0.2 g), and NaClO_4 (0.2 g) in methanol (8 ml) was heated at 60° for 5 min to give the pale yellow salt *K* (0.23 g) which was recrystallised from acetone–light petroleum (60—80°).

$[\text{Rh}_3\text{O}(\text{CO}_2\text{Me})_6(\beta\text{-pic})_3]\text{ClO}_4$ (*L*).—By addition of β -picoline to a water solution of *M*, the yellow salt *L* was precipitated. Both *K* and *L* are soluble in pyridine, CH_3CN , DMSO, DMF, CHCl_3 , and CH_2Cl_2 , slightly soluble in acetone and alcohols and insoluble in ether, light petroleum, benzene, CCl_4 , acetic acid, and water.

$[\text{Rh}_3\text{O}(\text{CO}_2\text{Me})_6(\text{PPh}_3)_3]\text{ClO}_4$ (*N*).—A mixture of *M* (0.16 g) and triphenylphosphine (0.48 g) in methanol (20 ml) was heated at 60° for 5 h under N_2 to give the red-orange solution. Removal of solvent left a residue (0.63 g) which was washed with ether, leaving a red-orange solid *N* (0.31 g). Recrystallisation from ethanol gave pure *N* (0.23 g). Very soluble in CH_2Cl_2 , CHCl_3 , pyridine, CH_3NO_2 , DMF, DMSO, CH_3CN , and acetone, slightly soluble in alcohol, ethyl acetate, and insoluble in water, ether, light petroleum, and CCl_4 .

$[\text{Ir}_3\text{O}(\text{CO}_2\text{Me})_6(\text{H}_2\text{O})_3]\text{CO}_2\text{Me}$ (*O*).—An acetic acid (50 ml) solution of iridium trichloride hydrate (1 g) and silver acetate (2 g) was heated under reflux for 3 h. The silver chloride formed was filtered off and the filtrate was evaporated to dryness to give a green residue. This residue was extracted with methanol to remove unreacted silver acetate and removal of solvent left green *O* (0.70 g). Soluble in alcohols, acetic acid, water, and pyridine, insoluble in CH_2Cl_2 , CCl_4 , ether, light petroleum, benzene, and acetone. The complex *O* was also obtained from 'chloroiridic acid' and silver acetate in acetic acid under reflux for 6 h.

$[\text{Ir}_3\text{O}(\text{CO}_2\text{Me})_6(\text{H}_2\text{O})_2(\text{MeCO}_2\text{H})](\text{CO}_2\text{Me})_2$ (*P*).—The green acetic acid (250 ml) solution of *O* (2.3 g) was ozonised at refluxing temperature for 24 h to give a deep blue solution. Removal of solvent left crude blue *P*. This crude product was dissolved in methanol and filtered and then ether was added to afford the deep blue *P* (1.8 g). I.r. spectrum and the solubilities are almost identical with those of *O*.

$[\text{Ir}_3\text{O}(\text{CO}_2\text{Me})_6(\text{H}_2\text{O})_2(\text{MeCO}_2\text{H})]\text{CO}_2\text{Me}$ (*Q*).—The dark blue aqueous solution of *P* (0.4 g, 150 ml) containing sodium perchlorate (0.61 g) was reduced electrochemically at -0.5 V vs. s.c.e. using a platinum foil electrode for 5 h at room temperature to give a brown solution from which the pale green *Q* (0.3 g) was precipitated by the addition of an excess of acetone. I.r. spectrum and the solubilities are almost identical with those of *O*. The complex *R* was precipitated by heating the brown solution with pyridine at 80° for 1 h.

$[\text{Ir}_3\text{O}(\text{CO}_2\text{Me})_6(\text{py})_3]\text{ClO}_4$ (*R*).—A mixture of *P* (0.4 g), pyridine (0.5 g), and $\text{NaClO}_4\cdot\text{H}_2\text{O}$ (0.5 g) in ethanol (20 ml) was heated under reflux. The yellow solid *R* formed was collected (0.2 g) and washed with ethanol and ether. Similar treatment using *O* (0.8 g) gave *R* (0.4 g).

$[\text{Ir}_3\text{O}(\text{CO}_2\text{Me})_6(\beta\text{-pic})_3]\text{ClO}_4$ (*S*).—A similar procedure using *P* (0.2 g) and β -picoline in ethanol (10 ml) gave yellow *S* (0.1 g). From the reaction with *O* (0.2 g), *S* (0.05 g) was obtained. Both *R* and *S* are soluble in CHCl_3 , acetone, CH_3CN , and CH_3NO_2 , slightly soluble in alcohols, acetic acid, and benzene, and insoluble in ether, water, and CCl_4 .

$[\text{Ir}_3\text{O}(\text{CO}_2\text{Me})_6(\text{py})_3](\text{ClO}_4)_2$ (*T*).—A suspension of *R* (0.1 g) in acetone (50 ml), containing sodium perchlorate (0.61 g), was oxidised electrochemically at $+1.0$ V vs. s.c.e. using

platinum foil electrode for 20 h at room temperature to give a blue precipitate of *T* which was collected (0.1 g) and washed with acetone and ether. Soluble in DMF, DMSO, CH_3CN , and CH_3NO_2 , slightly soluble in methanol, acetone, acetic acid, pyridine, CHCl_3 , and CH_2Cl_2 , and insoluble in ether, ethanol, benzene, and light petroleum.

$[\text{Ir}_3\text{O}(\text{CO}_2\text{Me})_6(\text{PPh}_3)_3](\text{CO}_2\text{Me})_2$ (*U*).—The deep blue methanol (15 ml) solution of *P* (0.2 g) and triphenylphosphine (0.2 g) was stirred under N_2 at room temperature for 20 h to give a light blue solid (0.06 g), *U*. More *U* (0.04 g) was obtained by cooling the filtrate. Soluble in alcohols, acetone, acetic acid, CH_2Cl_2 , and CHCl_3 and insoluble in ether, CCl_4 , and light petroleum.

Ozonisation of Other Metal Acetates.—Ozone was bubbled through a refluxing acetic acid (250 ml) solution of one of the following salts for ca. 30 h: $\text{Ni}(\text{CO}_2\text{Me})_2 \cdot 4\text{H}_2\text{O}$ (5 g), $\text{Cu}(\text{CO}_2\text{Me})_2 \cdot \text{H}_2\text{O}$ (2 g), $\text{Mo}_2(\text{CO}_2\text{Me})_4$ (1 g), $\text{Pd}(\text{CO}_2\text{Me})_2$ (1 g), AgCO_2Me (1.7 g), $\text{Pt}(\text{CO}_2\text{Me})_2$ (0.5 g). I.r. spectra of the

residues obtained by evaporation of solvent to dryness were quite similar to those of the corresponding starting metal acetates except for molybdenum(II) acetate. In the latter case molybdenum oxide (MoO_3) was formed. The addition of pyridine and sodium perchlorate to ethanolic solutions of the residues did not give the desired products; Cu^{II} , Pd^{II} , and Pt^{II} gave only the tetrapyridine complex salts $[\text{M}(\text{py})_4](\text{ClO}_4)_2$.

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¹⁸ P. Legzdins, R. W. Mitchell, G. L. Rempel, J. D. Ruddick, and G. Wilkinson, *J. Chem. Soc. (A)*, 1970, 3322.