Hexachloro-metallates: Infrared, Nuclear Quadrupole Resonance Spectra, and *X*-Ray Structural Studies

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A solid-state study of tervalent hexachloro-complexes R_3MCl_6 (M = Rh or Ir) and quadrivalent hexachloro-complexes R_2MCl_6 (M = Mn, Tc, Ru, and Rh) has been carried out by use of *X*-ray, n.q.r., and i.r. techniques. The ^{35}Cl n.q.r. spectra of the complexes K_3RhCl_6,H_2O, K_3IrCl_6,H_2O, K_3IrCl_6, and $(NH_4)_3IrCl_6,H_2O$ are complex and suggest a low site-symmetry for the anion. This is verified from the low-frequency i.r. spectra of the compounds and a full single-crystal *X*-ray analysis of K_3RhCl_6,H_2O. The latter complex is orthorhombic and has space-group *Pbcn* with 8 molecules $Z = 8$ in a unit cell of dimensions $a = 1{\cdot}2368(9)$, $b = 1{\cdot}5655(6)$, and $c = 1{\cdot}2041(10)$ nm. The structure was solved from diffractometer data and refined R 0·07 for 920 independent reflexions. The octahedral $RhCl_6^{3-}$ anions contain six crystallographically independent Rh–Cl bonds ranging in length from 230·2(4) to 236·6(4) pm. The lack of symmetry in the anion appears to be influenced by the neighbouring molecule of water of crystallisation. The n.q.r. spectra of the cubic octahedral quadrivalent complexes R_2MCl_6 (M = Mn, Tc, Ru, or Rh) have been measured and display the same trends as observed previously for the metal hexachloro-complexes of the third transition-series.

STUDIES of the hexachloro-complexes of the heavy transition-metals have been generally restricted to the quadrivalent complexes R_2MCl_6 of the third transition-metal series. We report i.r. spectra, n.q.r., and *X*-ray structural studies on the tervalent complexes of rhodium and iridium and quadrivalent complexes R_2MCl_6 of some of the second-row transition-metals.

The tervalent complexes have been investigated previously by means of i.r.[1,2] and u.v.–visible spectroscopy.[3,4] There is, however, some confusion over the stoicheiometry of the complexes.[2] The compounds differ from the cubic K_2PtCl_6 structural types of the R_2MCl_6 complexes in that in the solid state their structures are more complex, especially when the compounds are associated with a molecule of water, as in K_3RhCl_6,H_2O. The low-frequency i.r. spectra of some of the complexes reported previously bear this out.[1,2]

The quadrivalent hexachloro-complexes of the second-row transition-metals are normally assumed to be similar to those of the related members of the third transition-metal series. The present n.q.r. and i.r. studies show this to be a reasonable assumption in broad outline but certain significant differences in the metal–chlorine bond are now apparent. Several studies of the n.q.r. spectra of the hexachloro-complexes of the third-row transition-metals have been reported,[5-7] the most

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[1] D. M. Adams and H. A. Gebbie, *Spectrochim. Acta*, 1963, **19**, 925.

[2] P. J. Hendra and P. J. D. Park, *Spectrochim. Acta*, 1967, **23**, *A*, 1635.

[3] C. J. Jorgensen, *Acta Chem. Scand.*, 1956, **10**, 500.

[4] C. K. Jorgensen, *Acta Chem. Scand.*, 1957, **11**, 151.

[5] M. Kubo and D. Nakamura, *Adv. Inorg. Chem. Radiochem.*, 1966, **8**, 257, references therein.

[6] T. L. Brown, W. G. McDugle, and L. G. Kent, *J. Amer. Chem. Soc.*, 1970, **92**, 3645.

[7] T. L. Brown and L. G. Kent, *J. Phys. Chem.*, 1970, **74**, 3572.

pertinent to the present work being those of Nakamura and Kubo and co-workers [5] and Brown and co-workers.[6,7] Revealing comparisons can now be made between the complexes of the second- and third-row transition-metal series.

RESULTS

The hexahalogeno-complexes studied in the present work are listed in Table 1 together with their analytical data. All the compounds were made by reported methods except for K_2RuCl_6 (see Experimental section).

TABLE 1

Analytical data

	% Cl	
	Found	Calc.
$Na_3RhCl_6,10H_2O$ [a]	36·8	37·7
$Na_3RhCl_6,2H_2O$ [a]	51·0	50·6
K_3RhCl_6,H_2O [a]	47·2	47·2
K_3RhCl_6 [b]	49·0	49·2
Cs_2RhCl_6 [c]	35·8	36·6
K_3IrCl_6,H_2O [d]	39·1	39·4
K_3IrCl_6 [b]	41·0	40·8
$(NH_4)_3IrCl_6,H_2O$ [d]	44·2	44·6
$(NH_4)_3IrCl_6$ [b]	45·4	46·4
K_2RuCl_6 [b]	53·6	54·3
Cs_2MnCl_6 [e]	38·8	39·95
K_2MnCl_6 [e]	60·5	61·51

The references are to the methods of preparation:

[a] G. B. Kauffman and J. H. Tsai, *Inorg. Synth.*, 1966, **8**, 217. [b] See Experimental section. [c] Ref. 9. [d] I. A. Poulsen and C. S. Garner, *J. Amer. Chem. Soc.*, 1962, **84**, 2032. [e] Ref. 9.

(a) *Nuclear Quadrupole Resonance* (^{35}Cl).—*Iridium compounds.* The tervalent iridium complexes all show complex n.q.r. spectra. The lines are labelled for ease of discussion and is not meant to imply that the origin of the lines remain unchanged throughout the temperature range.

(i) K_3IrCl_6,H_2O. The resonance pattern of this compound consisted of six well spaced lines of roughly equal intensity, at frequencies shown in Table 2. The lines behaved quite regularly with temperature, all increasing, at slightly different rates, in intensity and frequency as the temperature was reduced towards 201 K. The resonances became very weak at 77 K. The mean frequency at 298 K is 17·73, and at 201 K 17·80 MHz.

TABLE 2

^{35}Cl N.q.r. frequencies (MHz) for K_3IrCl_6,H_2O

	(a)	(b)	(c)	(d)	(e)	(f)
298 K	16·754	16·939	17·505	18·109	18·251	18·800
S/N *	9	10	10	12	10	11
243 K	16·773	16·968	17·533	18·144	18·289	18·863
S/N	10	11	13	16·5	17·5	12·5
201 K	16·739	16·998	17·562	18·179	18·323	18·927
S/N	14	21	18	16	21	18
$\frac{d\nu}{dT}$ (kHz deg^{-1} at 298 K)	−0·3	−0·5	−0·5	−0·6	−0·7	−1·1

* S/N = Signal-to-noise ratio for time constant of 10 s.

(ii) K_3IrCl_6. The n.q.r. pattern of this compound showed very complex behaviour with temperature (Table 3). None of the resonance lines was detectable at 77 K. Those resonances observed at sufficient temperature points, *i.e.* (d), (e), and (f), showed linear frequency-dependence on temperature, and it is assumed the others have a similar dependence. The frequencies of lines (b) and (c) may be extrapolated to 298 K, and the mean of all frequencies at this temperature is then 17·56 MHz. The unweighted mean of the resonance actually observed at 298 K is 17·65 MHz while the averages of resonances observed at 222 and 201 K are 17·81 and 17·82 MHz. Regardless of the method of averaging, it is clear that the mean frequency for K_3IrCl_6 is very much the same as for K_3IrCl_6,H_2O, and the spread of frequencies is very similar in the two compounds.

TABLE 3

^{35}Cl N.q.r. frequencies (MHz) for K_3IrCl_6

	(a)	(b)	(c)	(d)	(e)	(f)
298 K	16·639			17·690	17·845	18·435
S/N *	24			10	7·5	7·5
273 K	16,648			17·712	17,864	18,468
S/N	7·5			6	7	7·5
243 K				17·733	17·874	18·502
S/N				6·5	4·5	6·5
222 K		17·378	17·508	17·753	17·890	18·527
S/N		8	7·5	5·5	3·5	8·0
201 K		17·403	17·521			18·558
S/N		18·5	24·5			6
$\frac{d\nu}{dT}$ † (kHz deg.$^{-1}$)	−0·4	−1·2	−0·6	−0·9	−0·8	−1·3

* S/N = Signal-to-noise ratio for time constant of 30 s.
† At 298 K or nearest temperature where line appears.

(iii) $(NH_4)_3IrCl_6,H_2O$. The n.q.r. pattern of this compound (Table 4) was also very complex, and consisted of five resonances. It is possible that one resonance escaped detection or resolution. At 77 K, only four lines were observed, and the assignments of these (Table 4) were based on linear extrapolation from 201 K. It is possible that line (e) could overlap with line (c) at 77 K. At all other temperatures, five lines were observed, with roughly equal intensities. Lines (b)—(e) showed negative temperature coefficients while (a) showed a small positive temperature

TABLE 4

^{35}Cl N.q.r. frequencies (MHz) for $(NH_4)_3IrCl_6,H_2O$

	(a)	(b)	(c)	(d)	(e)
298 K		17·526		17·758	18·038
S/N *		10		8	8
273 K	17·559	17·610	17·704	17·847	18·069
S/N	9	11	9	8	8
243 K	17·539	17·672	17·780	17·902	18·084
S/N	8	11	9	9	9
222 K	17·527	17·722	17·831	17·954	18·096
S/N	10	11	10	10	10
201 K	17·522	17·773	17·868	18·016	18·102
S/N	14	12	13	11	14
77 K	17·498	18·056	18·165	18·283	
S/N	9	7	9	10	
$\frac{d\nu}{dT}$ † (kHz deg.$^{-1}$ at 298 K)	+0·7	−3·4	−3·8	−3·6	−1·2

* S/N = Signal-to-noise ratio for time constant of 10 s.
† At 298 K or nearest temperature where line appears.

coefficient. The unweighted mean of frequencies observed at 201 K was 17·86 MHz, while, if lines (a) and (c) are extrapolated to 298 K, the mean frequency at 298 K is 17·71 MHz. The mean frequency and the spread of frequencies is very similar to those found for K_3IrCl_6,H_2O, and if a sixth resonance escaped detection it is predicted that it would be close to 17·7 MHz.

Rhodium compounds. The n.q.r. data observed for some rhodium compounds is shown in Table 5. Three relatively weak resonances were observed for K_3RhCl_6,H_2O at 298 K. The two outer lines disappeared below 243 K, and thereafter, the remaining line grew to moderate intensity. The mean frequency of the resonances observed at room temperature is 18·76 MHz, slightly higher than that of the line below 243 K, and *ca.* 1 MHz higher than the frequencies observed in two other tervalent rhodium compounds. $Na_3RhCl_6,2H_2O$ and $Na_3RhCl_6,10H_2O$ each showed a single resonance line, the frequencies and negative temperature coefficients being very similar. The compound Cs_2RhCl_6 showed a single resonance at all temperatures, with a rather small negative temperature coefficient. The resonance showed small changes in both frequency and intensity over a period of some weeks, presumably due to reduction to the tervalent state which occurs rapidly in solution.[8] The reported frequency and intensity is for freshly prepared compound. No resonances were detected for the following compounds: $(NH_4)_3RhCl_6,H_2O$, Rb_3RhCl_6, Cs_3RhCl_6, $(Me_4N)_3RhCl_6$, K_3RhCl_6, $(NH_4)_3RhCl_6$, and Rb_3IrCl_6.

TABLE 5

^{35}Cl N.q.r. frequencies (MHz) for rhodium compounds

T/K	K_3RhCl_6,H_2O	S/N *	$Na_3RhCl_6,2H_2O$	S/N †	$Na_3RhCl_6,10H_2O$	S/N †	Cs_2RhCl_6	S/N †
298	(a) 18·292	7	17·618	12	17·664	32	21·859	11
	(b) 18·497	9						
	(c) 19·463	8						
273	(a) 18·314	8					21·869	5
	(b) 18·514	10						
	(c) 19·493	8						
243	(q) 18·331	11	17·665	5	17·738	22		
	(b) 18·525	12						
	(c) 19·536							
231	18·536	14	17·687	6				
204	18·551	18						
201	18·555	19	17·702	7	17·794	16	21·908	6
183			17·709	5				
77					17·904	8		
$\frac{d\nu}{dT}$ (kHz deg.$^{-1}$ at 298 K)	(a) −0·8 (b) −0·6 (c) −1·2		−0·8		−1·3		−0·5	

* S/N = Signal-to-noise ratio for time constant of 30 s. † S/N = Signal-to-noise ratio for time constant of 10 s.

TABLE 6

^{35}Cl N.q.r. frequencies (MHz) for K_2RuCl_6, K_2MnCl_6, Cs_2MnCl_6, and K_2TcCl_6

Compound	*T*/K	Frequency/ MHz	S/N	d*ν*/d*T* (kHz deg^{-1} at 298 K)
K_2RuCl_6 [b]	298	17·345	7·5 [a]	−0·04
	259·5	17·347	9·5	
	232	17·349	10·5	
	200	17·349	10·5	
	172·5	17·350	9·0	
	150·5	17·352	7·0	
	122·5	17·352	4·5	
K_2MnCl_6	298	18·816	100 [d]	−0·12
	77	18·843	350—400 [c]	
Cs_2MnCl_6	298	19·516	8 [d]	−0·10
	77	19·539	60	
K_2TcCl_6 [b]	358·5	14·200	25 [d]	
	298	14·192	34	+0·15
	240	14·183	48	
	208	14·176	60	
	142	14·161	93	
	77	14·148	136	

[a] For time constant of 10 s. [b] See ref. 14. [c] After 70 h S/N = 70. [d] For time constant of 3 s.

Ruthenium compounds. The complex K_2RuCl_6 showed a single resonance at all temperatures measured (Table 6) down to 117 K. No resonances were detected for the tervalent complexes $K_2RuCl_5(H_2O)$ and $(NH_4)_2RuCl_5(H_2O)$.

Technetium complex. The complex K_2TcCl_6 showed a single resonance for the temperatures measured (Table 6).

Manganese compounds. The two complexes K_2MnCl_6 and Cs_2MnCl_6 show a single resonance with very high signal-to-noise ratios (Table 6). Over a period of time (72 h) the intensities were reduced to *ca.* 1/3 and 2/3 the original value respectively but the frequencies did not change. The drop is associated with compound decomposition.[9]

(b) *Infrared Spectra.*—The low-frequency spectra (400—40 cm^{-1}) of a number of the complexes were recorded and absorption maxima are listed in Table 7. The spectra consist of three regions of absorption *viz.*: *ca.* 320, *ca.* 180, and *ca.* 100 cm^{-1}. The first absorption region is associated with the metal–chlorine assymetric stretch (ν_3). In a number of cases, particularly compounds associated with water, the peak is more complex than a single absorption indicating that the symmetry of the anion is lower than octahedral in the solid state. The second absorption region is in the position expected for the Cl–M–Cl bending frequency (ν_4) and the low-energy absorption, which is often broad, is probably a lattice mode.

(c) X-*Ray Powder Photographs.*—Comparison of *X*-ray powder photographs indicated isomorphism between the pairs of compounds: K_3RhCl_6,H_2O and K_3IrCl_6,H_2O; K_3RhCl_6 and K_3IrCl_6; and Cs_2RhCl_6 and Cs_2IrCl_6. The complexes K_2MnCl_6, Cs_2MnCl_6,[9] K_2RuCl_6, and K_2TcCl_6,[10] all have the K_2PtCl_6 structure.

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[8] I. Feldman, R. S. Nyholm, and E. Watton, *J. Chem. Soc.*, 1965, 4724.

[9] P. C. Moews, *Inorg. Chem.*, 1966, **5**, 5.

[10] M. Elder, J. E. Fergusson, G. J. Gainsford, J. H. Hickford, and B. R. Penfold, *J. Chem. Soc.* (*A*), 1967, 1423.

TABLE 7

I.r. vibrational frequencies (cm^{-1})

	ν_3	ν_4	Lattice mode
Cs_2IrCl_6	321	182·5	72·5
Cs_2RhCl_6	334	185·0	80·0, 72·5
K_2IrCl_6	334	182·5	85·0
$K_3IrCl_6H_2O$	(310), 299, (285)	184br	110 (br, 120—90)
K_3IrCl_6	310 ,(305), (285)	185br	110
$(NH_4)_3IrCl_6,H_2O$	302·5, 292·5	197 (br, 220—177)	132 (br, 137—130)
$(NH_4)_3IrCl_6$	302·5	200 (br, 210—187)	131 (br, 142—120)
$Na_3RhCl_6,10H_2O$	318, 310	172br	135?
$Na_3RhCl_6,2H_2O$	321, 310	212br	157?, 90?
K_3RhCl_6,H_2O	328, 305, 277?	200w	110br
K_3RhCl_6	321br, 300	?	120 (br, 132—110)
K_2OsCl_6	(334), 325	177·5	85·0
K_2RuCl_6	(345), 337·5	185	87·5
K_2TcCl_6 [a]	327		

[a] Ref. 10.

(d) *Crystal Structure of* K_3RhCl_6,H_2O.—The structure (Figure 1) consists of discrete $RhCl_6^{3-}$ anions arranged in chains with channels between them containing K^+ ions and water molecules. Atom parameters and interatomic distances and angles are given in Tables 8—11.

TABLE 8

Atomic co-ordinates for K_3RhCl_6,H_2O expressed as fractions of the crystal unit-cell edges

Atom	x	y	z
Rh	0·21481(8) [a]	0·12890(7)	0·05731(9)
Cl(1)	0·3472(3)	0·1337(2)	0·1988(3)
Cl(2)	0·0783(3)	0·1282(2)	−0·0778(3)
Cl(3)	0·2861(3)	0·2551(2)	− 0·0193(3)
Cl(4)	0·1417(3)	0·0045(2)	0·1340(3)
Cl(5)	0·0987(3)	0·2065(2)	0·1675(3)
Cl(6)	0·3278(3)	0·0452(2)	−0·0580(3)
K(1)	0·1087(3)	0·0752(2)	0·3838(3)
K(2)	0·2686(3)	0·3329(2)	0·2334(3)
K(3)	0·4635(3)	0·1643(2)	0·4729(3)
O	0·0894(9)	0·4309(7)	0·1654(10)

[a] Here and in later Tables the figures in parentheses are estimated standard deviations in the least significant digits quoted.

TABLE 9

Root-mean-square components (pm) of thermal displacement of atoms in K_3RhCl_6,H_2O along principal axes of their vibration ellipsoids

Atom	Axis (1)	Axis (2)	Axis (3)
Rh	12·7(2)	14·1(3)	16·2(2)
Cl(1)	16·2(7)	19·0(6)	22·0(6)
Cl(2)	16·1(7)	17·2(6)	20·3(6)
Cl(3)	15·3(7)	18·5(6)	22·6(6)
Cl(4)	13·1(8)	17·9(6)	20·6(6)
Cl(5)	14·3(7)	17·7(6)	20·8(6)
Cl(6)	15·0(8)	21·2(6)	23·3(6)
K(1)	17·5(6)	17·9(6)	20·6(5)
K(2)	16·3(7)	19·9(6)	31·3(6)
K(3)	17·6(6)	25·9(5)	28·5(6)
O	25(2) [a]		

[a] Root-mean-square radial displacement for atom treated isotropically.

(e) *Differential Thermal Analysis*.—The complexes K_3RhCl_6,H_2O, K_3IrCl_6, and K_3IrCl_6,H_2O were studied by differential thermal analysis over the temperature range 273—200 K. The results are tabulated in Table 12. Discontinuities in the e.m.f. on cooling are taken as indicating a phase change. All the discontinuities occurred in the reverse direction on warming the sample.

TABLE 10

Bond lengths (pm) and angles (deg.) in the $RhCl_6^{3-}$ ion in K_3RhCl_6,H_2O *

(*a*) Bonds

Rh–Cl(1)	236·4(4)	Rh–Cl(4)	233·7(4)
Rh–Cl(2)	234·5(4)	Rh–Cl(5)	230·2(4)
Rh–Cl(3)	235·2(4)	Rh–Cl(6)	236·6(4)

(*b*) Angle †

Cl(1)–Rh–Cl(2)	177·3	Cl(2)–Rh–Cl(6)	90·9
Cl(1)–Rh–Cl(3)	89·8	Cl(3)–Rh–Cl(4)	179·2
Cl(1)–Rh–Cl(4)	90·6	Cl(3)–Rh–Cl(5)	91·0
Cl(1)–Rh–Cl(5)	90·0	Cl(3)–Rh–Cl(6)	90·8
Cl(1)–Rh–Cl(6)	91·8	Cl(4)–Rh–Cl(5)	88·3
Cl(2)–Rh–Cl(3)	90·1	Cl(4)–Rh–Cl(6)	89·9
Cl(2)–Rh–Cl(4)	89·5	Cl(5)–Rh–Cl(6)	177·5
Cl(2)–Rh–Cl(5)	87·3		

* Estimated standard deviations of individual measurements were calculated using variances and covariances in positional parameters and variances only in cell parameters. † All angles have estimated standard deviations of *ca.* 0·1°.

TABLE 11

Intermolecular contacts <370 pm with the chlorine atoms in the $RhCl_6^{3-}$ ion in K_3RhCl_6,H_2O

Cl(1) ··· K(3)	316	Cl(4) ··· K(2)	314
Cl(1) ··· K(2)	329	Cl(4) ··· K(1)	323
Cl(1) ··· O	330	Cl(4) ··· K(1)	329
Cl(1) ··· K(3)	363	Cl(4) ··· K(1)	330
		Cl(4) ··· Cl(2)	349
Cl(2) ··· K(2)	302	Cl(4) ··· O	354
Cl(2) ··· K(1)	324		
Cl(2) ··· K(3)	334	Cl(5) ··· K(2)	299
Cl(2) ··· K(1)	339	Cl(5) ··· K(3)	319
Cl(2) ··· Cl(4)	349	Cl(5) ··· K(1)	332
		Cl(5) ··· K(1)	334
Cl(3) ··· K(1)	318	Cl(5) ··· O	352
Cl(3) ··· K(2)	328		
Cl(3) ··· K(3)	334	Cl(6) ··· K(3)	335
Cl(3) ··· K(2)	335	Cl(6) ··· K(2)	338
Cl(3) ··· K(3)	345	Cl(6) ··· K(1)	338
		Cl(6) ··· O	339
		Cl(6) ··· O	350

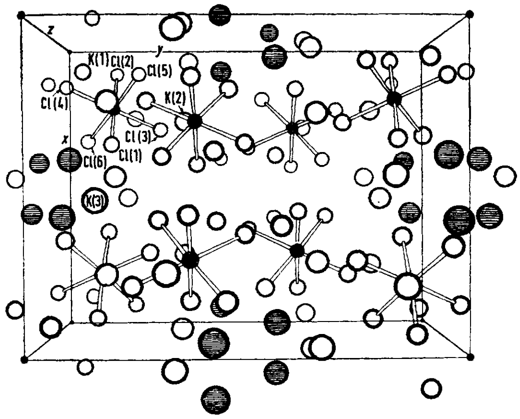

FIGURE 1 A perspective view of the unit-cell contents of K_3RhCl_6,H_2O viewed down the c axis. Shaded circles represent water molecules. Open circles not connected to Rh atoms represent potassium ions

TABLE 12

Differential thermal analysis data

K_3RhCl_6,H_2O		K_3IrCl_6		K_3IrCl_6,H_2O	
T/K	E.m.f.	T/K	E.m.f.	T/K	E.m.f.
213	0·012	273	0·014	273	*ca.* 0
223	0·015	265	0·014	265	0·005
229	0·020	260	0·024	260	0·010
232	0·031	258	0·050	255	0·013
234	0·032	255	0·088 *	250	0·019
236	0·034	253	0·050	245	0·020
238	0·036 *	250	0·014	240	0·019
240	0·010	245	0·030	235	0·018
242	0·006	240	0·045	230	0·020
244	0·007	235	0·080 *	225	0·021
248	0·055	230	0·053	220	0·022
		225	0·020	215	0·020
		220	0·007	210	0·020
		215	0·008	205	0·019
		210	0·005		
		205	*ca.* 0		

* Discontinuities.

DISCUSSION

(a) *Tervalent Compounds*. (i) K_3RhCl_6,H_2O. Table 10 lists the six independent Rh–Cl bond distances in the $RhCl_6^{3-}$ anion and the angles subtended at the Rh atom by all pairs of Cl atoms. There are some significant deviations from the idealised octahedral symmetry, most notably in the lengths of the Rh–Cl bonds which range from 236·6(4) to 230·2(4) pm. These variations may be attributed to the different intermolecular environments of the six Cl atoms and in particular to the situation of the water molecule. This can be noted from the list of Cl atom contacts (Table 11).

Although actual anion symmetry is close to octahedral the site-symmetry is C_1, *i.e.* no symmetry at all. This means the degeneracy of the asymmetric stretching mode t_{1u} will be completely destroyed and one may expect up to three i.r.-active ν(M–Cl) vibrations. In addition, the symmetric stretch a_{1g} may, under these conditions, become i.r.-active. The degree of band splitting will however, depend on the completeness of the destruction of symmetry which depends on the magnitude of the intermolecular forces compared to the bonding forces in the $RhCl_6^{3-}$ anion. The presence of two distinct bands at 328 and 305 cm^{-1} for K_3RhCl_6,H_2O is therefore not inconsistent with the structure. A weak band at 277 cm^{-1} may be associated with the Rh–Cl stretching vibration. The i.r. spectrum of K_3RhCl_6,H_2O reported earlier [2] is less well resolved than ours.

The n.q.r. spectrum of K_3RhCl_6,H_2O consists of three lines at room temperature. In view of the complex environment of the anion and the presence of the water molecule it is not meaningful to calculate the intermolecular forces and their effect on each chlorine and hence the electric field gradient. However, since the Rh–Cl bonding is the main contributor to the electric field gradient it is possible, in terms of a simple consideration of the Rh–Cl bond lengths, to predict the experimental n.q.r. pattern. The Rh–Cl bond lengths can be grouped as follows: Rh–Cl(5) 230·2; Rh–Cl(2), Rh–Cl(3), and Rh–Cl(4) 233·7—235·2; and Rh–Cl(1) and Rh–Cl(6) 236·4, 236·6 which could give rise to a three line spectrum, one [Cl(5)] at high frequency and two lines closer together at lower frequency. However, in view of the six different Rh–Cl bond lengths and lack of any crystallographic symmetry it is not unreasonable to expect a six- (perhaps five-) line spectrum. However, the complex relaxation behaviour of other compounds studies in this work suggests that it may be possible that we have not been able to observe three lines because of unfavourable relaxation conditions, and so the explanation given for the three-line spectrum, in terms of bond lengths, must remain in doubt. Unfortunately, the relative intensities of the observed lines are of no assistance as they are weak and temperature dependent.

(ii) *Remaining compounds*. Of the remaining compounds studied, the one of interest in relation to K_3RhCl_6,H_2O is K_3IrCl_6,H_2O, which is isomorphous and presumably has the same structure. The i.r. Ir–Cl stretching mode is complex with a main absorption at 299 cm^{-1} with shoulders on either side in agreement with a low site-symmetry. The chlorine n.q.r. spectrum has six lines all of approximately equal signal to noise ratio. Each line may correspond to each of the chlorines around the iridium. If this is so, it lends support to the possibility that relaxation effects are the reason for the three-line spectrum for the rhodium complex. It is of interest however, that the spectrum for K_3IrCl_6,H_2O has the appearance of the rhodium spectrum twice over [*i.e.* lines (*abc*) and (*def*)] and suggests that there are two independent $IrCl_6^{3-}$ anions in the crystalline state, each of which give the same n.q.r. spectrum as the rhodium complex, but shifted in frequency from each other because of differences in environment. Except for $(NH_4)_3IrCl_6$ the remaining compounds studied by i.r. all have complex Rh–Cl or Ir–Cl stretching frequencies. This suggests again a reduction from octahedral site-symmetry. The n.q.r. spectra of K_3IrCl_6 and $(NH_4)_3IrCl_6,H_2O$ are complex but are in agreement with a number of different crystallographic environments for the chlorine atoms. The deca- and di-hydrates of Na_3RhCl_6 give unexpected single-line n.q.r. spectra yet the ν(Rh–Cl) stretching mode is distinctly split into two bands (Table 7). It is difficult to reconcile these latter two experimental results. It seems unlikely that n.q.r. resonances are missing in view of the strength of the observed line.

Nuclear quadrupole resonance spectra. The behaviour of the n.q.r. resonances with temperature for the two compounds K_3RhCl_6,H_2O and K_3IrCl_6 could be interpreted as indicative of phase changes. For K_3RhCl_6,H_2O a phase transition may occur below 243 K in which all the chlorine atoms move on to equivalent sites with environments much the same as the chlorine site responsible for line (b) above 243 K. For K_3IrCl_6 a total of six resonances were observed. If the appearances and disappearance of resonances can be taken as being indicative of phase transitions, we can suggest three phase transitions: one associated with the disappearance of line (a) below 273 K, one with the disappearance of lines (b) and (c) above 222 K, and a third with the disappearance of lines (d) and (e) below 222 K. Throughout all these phase transitions, the chlorine atoms corresponding to line (f) remain relatively unaffected, the frequency of this line showing no discontinuities with temperature. Such a phenomenon has been observed before in other compounds.[11] However, because of the rapid changes in intensity with temperature for lines (a), (b), and (c), we cannot rule out the possibility that the observed behaviour is the result of complex relaxation phenomena which may render some resonances undetectable in certain temperature regions. Furthermore, we hesitate to use the observed intensity patterns to draw conclusions as to the number of chlorine atoms on equivalent sites.

Experimental data in support of the phase changes have been obtained from low temperature differential thermal analysis studies on K_3RhCl_6,H_2O, K_3IrCl_6, and K_3IrCl_6,H_2O. The rhodium complex shows an enthalpy change at *ca.* 235—238 K. The complex K_3IrCl_6 shows two similar enthalpy changes at *ca.* 255 and 235 K, but no change between 201—222 K. In each case the temperatures of the enthalpy changes correspond to the temperature ranges where the number of n.q.r. resonance lines change. The hydrated complex K_3IrCl_6,H_2O shows no enthalpy change over the temperature range 200—273 K in agreement with no change in the number of n.q.r. lines over the same range. These results lead us to believe that the change in n.q.r. spectrum with temperature is indicative of at least some phase changes.

I.r. spectra. The i.r. stretching mode (t_{1u}) of the tervalent complexes show the typical shift from rhodium to iridium due to the influence of mass. The typical shift to lower energy relative to the quadrivalent state is also observed. The influence of the cation is most clearly seen by the changes observed for the lattice mode, and in fact is a reason for assigning the absorption around 100 cm^{-1} to a lattice mode (Table 7). The bending mode $\nu_4(t_{1u})$ is difficult to detect for the rhodium complexes and in the case of K_3RhCl_6 is absent altogether. This marked difference to the iridium compounds has also been observed for other tervalent halogeno-complexes. As expected, and as a consequence of the low site-symmetry the bending mode is complex in structure and not like the sharp absorption found for cubic R_2MCl_6 complexes.

(b) *Quadrivalent Complexes.*—The n.q.r. frequencies for the quadrivalent complexes studied, together with a number of reported values for other complexes, and the mean value for tervalent rhodium and iridium compounds, are given in Table 13. It is clear from this Table that (i) the resonance frequency decreases with oxidation state, (ii) it decreases in going from the first- to the second- and third-row transition-metal series, and (iii) it decreases with *d* electron configuration. It is usual [5,6] to equate the resonance frequency with an expression containing terms for the σ-covalent and Cl→M π-bonding character of the metal–chlorine bond, *viz.*: $\nu = 54{\cdot}873[(1 - s)\sigma - \pi/2]$, where s is degree of s hybridization, σ is degree of σ-bonding, and π is degree of Cl→M π bonding. In using this equation the asymmetry parameter η is taken as zero although values as high as 0·3 would not affect the discussion. Furthermore, s is taken as zero, in accord with recent experimental data.[12,13]

TABLE 13

Summary of ^{35}Cl n.q.r. frequencies (298 K)

d Electron confign.	Transition-metal series		
	3rd	2nd	1st
d^6	Pt^{IV} 25·82[a] (K^+)	Pd^{IV} 26·55[b] (K^+)	
	Ir^{III} *17·65*[c] (K^+)	Rh^{III} *18·76* (K^+)	
d^5	Ir^{IV} 20·74[a] (K^+)	Rh^{IV} [21·1[d] (K^+)]	
	21·46[a] (Cs^+)	*21·86* (Cs^+)	
d^4	Os^{IV} 16·84[e] (K^+)	Ru^{IV} *17·35* (K^+)	
d^3	Re^{IV} 13·89[e] (K^+)	Tc^{IV} *14·19* (K^+)	Mn^{IV} *18·82* (K^+)
			19·52 (Cs^+)

[a] Taken from J. E. Fergusson and D. E. Scaife, *Austral. J. Chem.*, 1971, **24**, 1325. [b] R. L. Armstrong and D. F. Cooke, *Canad. J. Phys.*, 1969, **47**, 2165. [c] Italicized values obtained in this work. [d] Estimated figure. [e] Ref. 5.

σ *Bonding.* In view of the filled t_{2g} orbitals for the d^6 configuration no π bonding can take place. Therefore for the chloro-complexes of Pt^{IV}, Pd^{IV}, Ir^{III}, and Rh^{III} the resonance frequency is just related to the covalent σ bonding. The lower frequency for the Ir^{III} and Rh^{III} complexes compared to Pt^{IV} and Pd^{IV} (*i.e.* $\nu Rh^{III}/\nu Pd^{IV}$ 0·71, $\nu Ir^{III}/\nu Pt^{IV}$ 0·68) indicates a reduction in σ bonding and an increase in ionic bonding as the oxidation state of the metal decreases. This result is in agreement with a lowering of the M–Cl i.r. stretching frequency with oxidation state. The ratio ν(second transition-metal series)/ν(third transition-metal series) is 1·03 (Pd, Pt^{IV}) and 1·06 (Rh, Ir^{III}), which can be interpreted as slightly greater σ bonding for the metal ions of the second transition-series.

The high n.q.r. resonance frequency for the $MnCl_6^{2-}$ anion either corresponds to negligible π bonding or greater than usual σ bonding. In view of the smaller size of the Mn^{IV} ion, compared to the second- and third-row transition-metals, and therefore its greater electronegativity it seems unreasonable to completely ignore π bonding particularly as it is believed to be extensive for the related complex K_2ReCl_6. Therefore it would appear that the σ covalency is high for manganese(IV). This is not unexpected in view of the usual trends observed for the first- to the second- and third-row transition-metals.

π *Bonding.* As the number of *d* electrons fall so does the n.q.r. resonance frequency, this being taken as due to an increase in π bonding.[5] The change in frequency with d^n (n = 2—5) is approximately linear (Figure 2), and extrapolation to n = 6 gives a value of the n.q.r. frequency for $PdCl_6^{2-}$ and $PtCl_6^{2-}$ which is too low.

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[11] A. Sasane, D. Nakamura, and M. Kubo, *J. Magn. Resonance*, 1970, **3**, 76, and references therein.

[12] R. Bersohn and R. G. Shulman, *J. Chem. Phys.*, 1966, **45**, 2298.

[13] M. Rinneburg, H. Haas, and H. J. Hartman, *J. Chem. Phys.*, 1969, **50**, 3064.

This is in agreement with no π bonding for these quadrivalent metal ions.

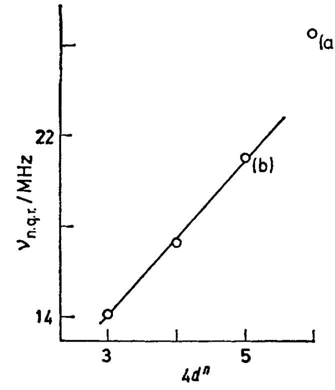

FIGURE 2 Variation in nuclear quadrupole resonance frequency with $4d^n$ for MCl_6^{2-} species; point (a) is taken from R. L. Armstrong and D. L. Cooke, *Canad. J. Phys.*, 1969, **47**, 2165; point (b) is estimated for K_2RhCl_6 from experimental value for Cs_2RhCl_6

One would expect that there is a maximum charge that the central metal ion can accept from the halogen by a π-bonding mechanism irrespective of the available bonding orbitals. This point has also recently been made by demonstrating a correlation between π bonding and optical electronegativity. A plot of n.q.r. frequency against d^n may therefore be curved. The fact that it is not suggests that the frequency is giving a measure of the total bonding and that changes in σ and π compensate each other. The approximate linear plot of ν_3 against d^n (Figure 3) suggests the same thing.

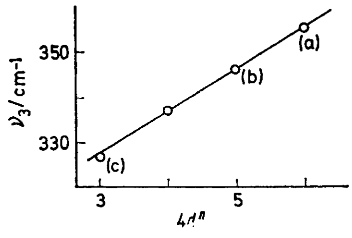

FIGURE 3 Variation in asymmetric (M–Cl) stretching frequency with $4d^n$ for MCl_6^{2-} species; point (a) is taken from P. Taimsalu and J. L. Wood, *Spectrochim. Acta*, 1964, **20**, 1943; point (b) is estimated for K_2RhCl_6 from experimental value for Cs_2RhCl_6; point (d) is taken from ref. 10

The temperature dependence of the ^{35}Cl n.q.r. frequency $(d\nu/dT)_P$ for the complexes A_2MCl_6 (M = Pd, Rh, Ru, and Tc) has recently been reported[14] and the results suggest that the π bonding is greater for the second-row transition-metals, especially for the electron configurations d^3 and d^4. The temperature coefficient of K_2MnCl_6 (Table 6) is comparable to those for the ruthenium and osmium complexes indicating less π bonding in the Mn–Cl bond than occurs for the heavier members of the Mn, Tc, Re triad. This is in agreement with the high value of the n.q.r. frequency for $MnCl_6^{2-}$ salts discussed.

Recently the π component of the metal–chlorine bond has been related to the optical electronegativity of the metal ion.[7] If both ν(n.q.r.) and ν_3 are plotted against $\chi_{opt.}$ straight lines are obtained in each case (Figure 4).

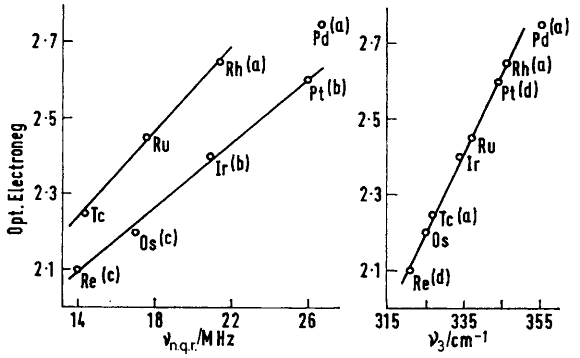

FIGURE 4 Variation in $\nu_{n.q.r.}$ and ν_3 with optical electronegativity for MCl_6^{2-} species; points (a) and (b) are as for Figures 2 and 3; points (c) are taken from ref. 5 and J. E. Fergusson and D. E. Scaife, *Austral. J. Chem.*, 1971, **24**, 1325; and points (d) from D. M. Adams, ' Metal–Ligand and Related Vibrations,' Arnold, London, 1967, p. 64.

However, for the ν(n.q.r.)/$\chi_{opt.}$ plot two lines are obtained one line for the second-row transition-metals and one for the third-row transition-metals. In terms of the optical electronegativity one would expect therefore a greater value of ν(n.q.r.) for the second-row transition-metals than observed. The low values may again suggest that the π bonding is greater for the second-row transition-metals. The calculated values of the π component of the bonding, using the equation derived by Brown and Kent[7] are given in Table 14. For comparison the values reported for Ir^{IV}, Os^{IV}, and Re^{IV} are 0·054, 0·081, and 0·097 respectively.

TABLE 14

	Pd^{IV}	Rh^{IV}	Ru^{IV}	Tc^{IV}
d_π holes	0	1	2	3
$\chi_{opt.}$ [a]	2·75	2·65	2·45	2·25
π [b]	0	0·93	0·118	0·130

[a] Values from C. K. Jorgensen, ' Halogen Chemistry,' vol. 1, Academic Press, New York, p. 265. [b] Calc. according to the equation: $\pi = 0{\cdot}054\ n(\Delta\chi_{Ir}/\Delta\chi_M)$, where $\Delta\chi_M = \chi_{opt.}{}^{M} - \chi_{opt}{}^{Cl}$ and $n = t_{2g}$ orbital vacancy (ref. 6).

The plot of $\nu_3/\chi_{opt.}$ puts all R_2MCl_6 compounds on the same straight line. However, if the mass of M is taken into consideration two lines will be obtained one for the second- and one for the third-row transition-metals in the same way as for the n.q.r. frequency.

In the foregoing discussions we have neglected the contribution to the field gradients at the chlorine atoms by point charges outside the complex ions, and by Sternheimer amplification of the polarization of the chlorine atom by charges external to the complex ions. The regularity of these results suggests that these effects are relatively minor, and roughly constant in the series

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[14] J. E. Ferguson and D. E. Scaife, *Inorg. Nuclear Chem. Letters*, 1971, **7**, 987.

studied. Evidence in favour of neglect of the Sternheimer factor has recently been put forward.[7]

EXPERIMENTAL

Preparation and Analyses.—The complexes were prepared by methods described in the literature. The anhydrous complexes K_3RhCl_6, K_3IrCl_6, and $(NH_4)_3IrCl_6$ were readily obtained from the mono-hydrate complexes by heating these to 120° for several hours. The ruthenium complex K_2RuCl_6 was prepared from commercial $RuCl_3,nH_2O$ by dissolution in concentrated hydrochloric acid and addition of potassium chloride. The resulting precipitate was principally $K_4[Ru_2OCl_{10}]$ which was reduced to $K_2RuCl_5(H_2O)$ with ethanol and then oxidised to K_2RuCl_6 with chlorine. The details of this preparative technique will be described in detail elsewhere. The chlorine content was estimated gravimetrically as AgCl. In the analyses of the iridium and ruthenium complexes it was first necessary to remove the metal as hydroxide as the addition of silver nitrate to an acidic solution of the complex anion MCl_6^{2-} gave preferentially Ag_2MCl_6 (M = Ru or Ir).

I.r. Spectra.—The i.r. spectra of the complexes were recorded as Nujol mulls by use of an RIIC Fourier transform spectrometer from 400—40 cm^{-1}. The spectra were checked by use of a Grubb Parsons DM 4 (over the region 500—200 cm^{-1}).

X-*Ray Powder Photography*.—Powder photographs of the complexes were obtained with a Phillips Debye–Scherrer Camera by use of Cu-K_α radiation.

Crystal-Structure Analysis of K_3RhCl_6,H_2O.—*Crystallographic data*. K_3RhCl_6,H_2O, M 450·94, Orthorhombic, $a = 1{\cdot}2368(9)$, $b = 1{\cdot}5655(6)$, $c = 1{\cdot}2041(10)$ nm, Mo-$K_{\alpha,1}$ radiation, $\lambda = 70{\cdot}93$ pm, $U = 2{\cdot}331$ nm^3, $D_m = 2{\cdot}64$ (by flotation), $Z = 8$, $D_c = 2{\cdot}61$. μ(Mo-K_α) = 38·37 cm^{-1}; Space-group *Pbcn* uniquely determined from systematic absences. No molecular symmetry required.

The unit-cell constants for the compound as reported by Hendra and Park[2] are systematically smaller than the above values, the mean ratio between the two units being 1·16 which is the ratio of the wave lengths of Co-K_α and Cu-K_α radiation. No details were given and it would appear that an incorrect value for the wavelength was used.

The crystal was mounted on a Hilger and Watts four-circle automatic diffractometer in a random orientation. Cell constants with their estimated standard deviations were obtained by least-squares refinement of the setting angles of five reflections obtained at room temperature with Mo-$K_{\alpha,1}$ radiation, a description of the orientation of crystal being obtained at the same time in the form of a 3 × 3 matrix.

By use of zirconium-filtered Mo-$K_{\bar{\alpha}}$ radiation intensities were measured in bisecting mode with symmetric θ—2θ step scans, stepping 0·01° in θ. Scan ranges were 0·4° for reflections having $\theta \leqslant 20°$ and 0·5° for θ 20—23°. Background counts for 15 s were taken at each end of the scan. Counter aperture was 3·5 mm diameter, crystal mosaicity 0·2°, and tube take-off angle 3°. One form of data, comprising 1472 reflections with intensities above background, was measured and no attenuation was required for the strongest reflections. Standard errors were assigned by the formula $\sigma = \{\text{Scan} + \text{Background} + [p \times (\text{Integrated Count})]^2\}^{\frac{1}{2}}$ where p is a variable parameter, given the value 0·03 in the final weighting scheme. 920 reflections had intensities $>3\sigma$. The crystal used for data collection was almost spherical with diameter 0·2 mm. A spherical absorption correction was applied during the data processing.

Structure analysis and refinement. A three-dimensional sharpened Patterson synthesis showed the position of the rhodium atom with four possible orientations for an octahedral set of chlorine atoms. Partial trial least-squares refinements followed by electron-density difference maps established the chlorine positions uniquely and also showed the positions of the three potassium ions and the oxygen atom. Full-matrix least-squares refinement of all positional and isotropic thermal parameters then followed, using all 920 reflections for which $F^2 > 3\sigma(F^2)$.

In all least-squares calculations the function minimised was $\Sigma W(|F_o| - |F_c|)^2$ where $W = 4F_o^2/[\sigma(F_o^2)]$. Atomic scattering factors for rhodium, potassium, chlorine, and oxygen were taken from ref. 15, those for the first three being corrected for anomalous dispersion by use of values for $\Delta f'$ and $\Delta f''$ tabulated in ref. 16.

Convergence of the refinement with isotropic temperature factors gave R 0·112 and R' 0·082 (where $R' = [\Sigma W(|F_o| - |F_c|)^2/\Sigma W|F_o|^2]^{\frac{1}{2}}$. Then all atoms except oxygen were converted to a six-parameter anisotropic model and after further refinement R was 0·070 and R' 0·052. The highest peak in a final electron-density difference map was 1760 enm^{-3} which was 0·28 of the height of the original peak due to the oxygen atom. Final fractional atomic co-ordinates are given in Table 8; and root-mean-square components of atomic thermal displacement along principal axes of the vibrations ellipsoids in Table 9. The final values of the observed and calculated structure factors are listed in Supplementary Publication No SUP 20248 (2 pp, 1 microfiche).*

Computations were carried out on an IBM 360 44 computer with 128 K bytes of core storage using programs previously described.[17]

Nuclear Quadrupole Resonance.—These measurements were carried out by use of a super-regenerative oscillator and frequency-measurement methods described elsewhere.[18] The sample was contained inside a heavy-walled copper can surrounded by copper cooling coils through which nitrogen gas flowed from a boiler controlled by a temperature controller. For liquid nitrogen temperatures, the can was immersed in liquid nitrogen. The temperatures were calibrated at fixed points, and also be measurement of the chlorine n.q.r. frequency of a sample of $KClO_3$, by use of the frequency–temperature equations of Utton.[19] The temperatures quoted are believed to be accurate to ±0·3 °C, and while in favourable cases, our frequency accuracy is better than ±1 kHz, we claim an accuracy of ±4 kHz for all the resonance lines reported here.

Differential Thermal Analysis.—A two-compartment tube was placed inside a low-temperature cryostat. One side contained α-Al_2O_3 as reference the other the complex under study. Copper–Constanstan thermocouples were embedded in each sample and connected to a Cambridge slide-wire potentiometer 44244 3 with readability of 0·001 mV and a

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* For details of Supplementary Publications see Notice to Authors No. 7 in *J. Chem. Soc.* (*A*), 1970, Issue No. 20 (items less than 10 pp. will be supplied as full size copies).

[15] 'International Tables for *X*-Ray Crystallography,' vol. 3, Kynoch Press, Birmingham, 1962.

[16] D. T. Cromer, *Acta Cryst.*, 1965, **18**, 511.

[17] M. D. Brice, B. R. Penfold, W. T. Robinson, and S. R. Taylor, *Inorg. Chem.*, 1970, **9**, 362.

[18] D. E. Scaife, *Austral. J. Chem.*, 1971, **24**, 1753.

[19] D. B. Utton, *J. Chem. Phys.* 1967, **47**, 371.

Tinsley Galvanometer Sr 4 45 with a deflection of 5 mm/µV. The temperature was allowed to drop gradually but continuously (also for heating) and e.m.f. differences resulting between sample and reference were recorded against temperature. Measurements over a temperature range of *ca.* 100° took *ca.* 2 h.

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