410. *The Constitution of Peroxy-compounds of the Vanadium and the Chromium Group.*

By J. E. Fergusson, C. J. Wilkins, and J. F. Young.

Magnetic moments, infrared spectra, and *X*-ray powder photographs have been used to establish structural relationships amongst peroxy-compounds of the vanadium and the chromium group. Isomorphism of vanadium salts with tetraperoxychromates establishes their composition and structure. Compounds known to contain only peroxidic oxygen, *viz.*, salts having the tetraperoxy-anion, MO_8^{3-}, and adducts of chromium diperoxide, CrO_4, give a single strong infrared absorption, at 870—890 cm.$^{-1}$ for chromium compounds and at lower frequencies for salts of Group V metals. The adducts of chromium monoxide diperoxide, CrO_5, are distinguished by diamagnetism and by having a broadened composite infrared absorption in the region 915—945 cm.$^{-1}$. Evidence about the blue perchromate anion is consistent with the formulation $Cr_2O_{12}^{2-}$. The broad features of the various classes of compound are discussed.

Of the diverse peroxy-compounds of transition metals two chromium compounds alone, potassium tetraperoxychromate[1] and triamminechromium diperoxide,[2] have been subjected to complete structure determination. In both compounds the peroxy-groups are co-ordinated laterally rather than end-wise, so that co-ordination numbers of the chromium are eight and seven, respectively. Proceeding from these two compounds we have obtained structural evidence on other classes of peroxy-compound from infrared spectra, *X*-ray powder photographs, magnetic moments, and electrolytic conductivities. The present report deals with salts containing the tetraperoxy-anion, MO_8^{3-}, the diperoxy-anions of the chromium group, and some of the more stable adducts from the chromium peroxides.

Salts containing the Tetraperoxy-anion, MO_8^{3-}.—Isomorphism of salts K_3MO_8, known with M as chromium, niobium, and tantalum,[3] extends also to vanadium. It is more difficult to obtain the vanadium compounds of this class in a pure state, and compositions have been reported recently[4] as $K_3VO_8,2H_2O$, $K_6H_2V_2O_{16},H_2O$, and $(NH_4)_6H_2V_2O_{16},H_2O$. However, our preparations of the potassium and ammonium salts gave *X*-ray powder patterns almost identical with those of anhydrous potassium and ammonium tetraperoxychromate which are themselves isomorphous. The magnetic moment of 0·60 B.M. for potassium tetraperoxyvanadate is sufficiently low to indicate absence of unpaired electrons and confirms the quinquevalency of vanadium. In solution the tetraperoxyvanadates decompose too fast to permit measurement of electrolytic conductivity. The conductivities of the more stable chromium, niobium, and tantalum compounds have values corresponding to 3 : 1 electrolytes, confirming the existence of the peroxy-anions in solution as well as within the crystalline salts.

Infrared spectra of these salts show a characteristically strong absorption, which appears at 875, 853, 814, and 813·5 cm.$^{-1}$ in the potassium salts of chromium, vanadium, niobium, and tantalum, respectively. A weak higher-frequency absorption also occurs (Table 1) and with tetraperoxychromates a band at 670—674 cm.$^{-1}$ lies within the spectral range. The position of the strong band, though influenced by the nature of the metal, is fairly close to the bands (870—900 cm.$^{-1}$) shown by hydrogen peroxide and organic peroxides,[5] which suggests that it arises from stretching vibrations of the

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[1] Wilson, *Arkiv Kemi, Min., Geol.*, 1941, **15**, *B*, No. 5, 1; Stromberg and Brossett, *Acta Chem. Scand.*, 1960, **14**, 441.

[2] McLaren and Helmholtz, *J. Phys. Chem.*, 1959, **63**, 1279.

[3] Bohm, *Z. Krist.*, 1926, **63**, 319.

[4] Martinez and Rodriguez, *Anales real. Soc. españ. Fís. Quím.*, 1952, **14**, *B*, 388.

[5] Giguère, *J. Chem. Phys.*, 1950 **18**, 88; Shreve, Heether, Knight, and Swern, *Analyt. Chem.*, 1951, **23**, 282; Philpotts and Thain, *ibid.*, 1952, **24**, 638.

TABLE 1.

Properties of peroxy-compounds.

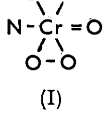
Compound	Peroxy-groups per metal atom	Magnetic moment (B.M.)	Oxidation level of metal	Infrared bands (cm.$^{-1}$)	Conductivity (ohm^{-1} mole^{-1} cm.^{2})
K_3CrO_8	4	1·77	5	975w, 875s, 675m	301·5 (H_2O, 5°)
$(NH_4)_3CrO_8$	4	1·77	5	970w, 870s, 665m	[a]
K_3VO_8	4	0·6 [b]	5	853s	[a]
$(NH_4)_3VO_8$	4	0·75 [b]	5	954w, 846s	[a]
K_3NbO_8	4	0·0	5	968w, 814s	380 (H_2O, 25°)
K_3TaO_8	4	0·0	5	968w, 813·5s	380 (H_2O, 25°)
$(NH_4)_2Cr_2O_{12},H_2O$	2·5	0·6 [b]	6	980s, 937s	67 (H_2O, 0°)
$KHMoO_6,2H_2O$	2	0·4 [b]	6	960s, 866w, 854s, 730s br	144 (H_2O, 25°)
$KHWO_6,2H_2O$	2	0·25 [b]	6	960s, 850m, 833s, 768s br	129 (H_2O, 25°)
$(NH_3)_3CrO_4$	2	2·8	4	891s	1·2 (H_2O, 5°)
$enCrO_4,2H_2O$	2	2·7	4	880s	Insoluble
$PyrCrO_5$	2	0·4 [b]	6	950w, 942w, 934s [c]	2·0 (DMF,[d] 16°)
$BipyrCrO_5$	2	0·6 [b]	6	947m, 925s [c]	5·0 (DMF, 16°)
1,10-$PhenCrO_5$	2	0·9 [b]	6	945m, 925s, 910w [c]	5·8 (DMF, 16°)

[a] In solution, decomposes too rapidly for measurement. [b] The small magnetic moments indicate absence of a " spin " component, and are probably due to temperature-independent paramagnetism. [c] The spectrum of the free base was obtained for comparison. [d] Dimethylformamide.

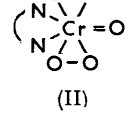
co-ordinated peroxy-groups. The neutral triamminechromium diperoxide, $(NH_3)_3CrO_4$, which resembles the tetraperoxy-salts in containing all its oxygen in similar peroxy-ligands,[2] shows the same strong infrared absorption.

Adducts from the Chromium Peroxides.—The two classes of adduct, those from chromium diperoxide, CrO_4, and chromium oxide diperoxide, CrO_5, which have been recognised on analytical grounds[6] show differing magnetic moments and infrared absorptions. Triamminechromium diperoxide and the ethylenediamine complex,[6d] for which analyses point to a composition $enCrO_4,2H_2O$, both have magnetic moments corresponding to two unpaired electrons and show the characteristic strong peroxy-absorption band. The spectrum of the latter compound shows in addition the band at 1640 cm.$^{-1}$ due to water, confirming the hydrated nature of this material. We interpret the magnetic moments of these compounds as indicating the chromium to be in the +4 oxidation state. The characteristic infrared absorption renders unlikely the alternative view of McLaren and Helmholz[2] that two superoxy-groups are co-ordinated to a chromium(II) centre.

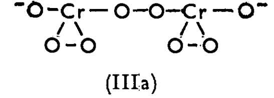
The adducts of chromium oxide diperoxide with pyridine, 2,2′-bipyridyl, and 1,10-phenanthroline, on the other hand, have low magnetic moments which show that they contain chromium(VI). That the compounds are neutral complexes rather than salts is confirmed both by their low electrolytic conductivities and by the absence of the N–H infrared stetching frequency. These spectra are characterised by a broadened composite band within the range 915—950 cm.$^{-1}$, which band may include a contribution from the Cr=O stretching absorption,[7] but the displacement of the characteristic peroxide band from the region 870—890 cm.$^{-1}$ suggests some interaction between the peroxy-groups and the oxide bond. Otherwise structures (I) and (II) seem adequate as formal representations of the compounds.



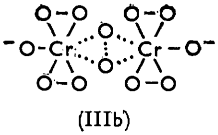
(I)



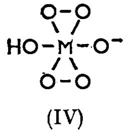
(II)



(IIIa)



(IIIb)



(IV)

The Blue Perchromates and the Protonated Diperoxy-anions, HMO_6^-, *of Molybdenum and Tungsten.*—The unstable blue perchromates have been variously formulated as containing

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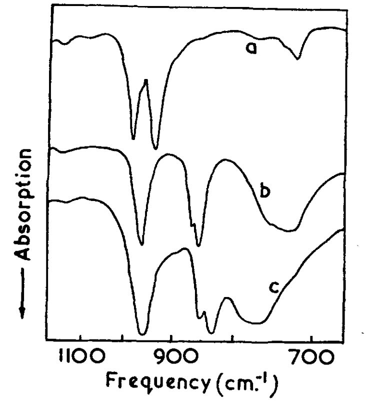
[6] Wiede, *Ber.*, (*a*) 1897, **30**, 2178; (*b*) 1898, **31**, 3139; Hofmann and Hiendlmaier, *Ber.*, (*c*) 1905, **38**, 3059; (*d*) 1906, **39**, 3181; (*e*) Riesenfeld, *Ber.*, 1905, **38**, 4068.

[7] Barraclough, Lewis, and Nyholm, *J.*, 1959, 3552.

anions $HCrO_6^-$,[8] CrO_6^-,[9] and $Cr_2O_{12}^{2-}$.[10] They resemble the more stable molybdenum and tungsten salts $KHMO_6,2H_2O$ [11] in forming in acid solution and in having no unpaired electrons, but the two classes of compound are otherwise different. Analysis of blue ammonium perchromate confirms the view that there can be no proton within the anion and that (subject to the validity of the method [10a] for determining peroxidic oxygen) there are close to 2·5 peroxy-groups per chromium atom. Two structural formulations are consistent with this evidence: (IIIa), due to Schwarz and Giese,[10a] and (IIIb) in which the peroxide bridge is co-ordinated laterally as in the μ-peroxycobalt complexes.[12] Both structures are compatible with the infrared spectrum. This contains two closely spaced strong absorptions which suggest the presence of peroxy-groups in two different environments, but otherwise has a simplicity which supports an equivalence of the two co-ordination centres in the binuclear ion.

The molybdenum and tungsten anions are well established as containing two peroxy-groups and a proton. Electrolytic conductivities of these salts are little higher than expected for a 1 : 1 electrolyte so that structure (IV) seems appropriate. Nevertheless the relatively complicated infrared spectra suggest there may be some structural complexity in the crystalline state. The strong water absorption at 1640 cm.$^{-1}$ persists in the vacuum-dried salts.



Infrared spectra of (*a*) blue ammonium perchromate, NH_4CrO_6,H_2O, (*b*) $KHMoO_6,2H_2O$, and (*c*) $KHWO_6,2H_2O$.

General Features of the Compounds.—Physical properties thus confirm the existence of the broad classes of peroxy-compounds which have been recognised on analytical evidence. Though infrared spectra give no ground to believe co-ordination of the peroxy-group to be other than through both oxygen atoms, the CrO_5 complexes with their modified spectra warrant closer structural study.

Formation of CrO_5-type adducts is favoured by heterocyclic bases, while ammonia and ethylenediamine produce derivatives of chromium diperoxide. It may be supposed that the stronger electron-donor properties of ammonia and the diamine initiate a degradation of chromium oxide diperoxide to the diperoxide, with consequent reduction in the oxidation level of the chromium, as in the preparation of triamminechromium diperoxide by treatment of the pyridine adduct with ammonia.[13,14] Triamminechromium diperoxide with chromium(IV) represents an intermediate in the series CrO_8^{3-}, $(NH_3)_3CrO_4$, $Cr(NH_3)_6^{3+}$ in which both the co-ordination number and the oxidation level fall progressively.

In the chromium peroxy-compounds whose structures have been determined the

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[8] Hofmann and Hiendlmaier, *Ber.*, 1904, **37**, 3405.

[9] Dwyer and Gibson, *Chem. and Ind.*, 1953, 153.

[10] (*a*) Schwarz and Giese, *Ber.*, 1933, **66**, 310; (*b*) Klemm and Werth, *Z. anorg. Chem.*, 1933, **216**, 127.

[11] Jahr and Lother, *Ber.*, 1938, **71**, 894.

[12] Brossett and Vannerberg, *Nature*, 1961, **190**, 714.

[13] Werner, *Ber.*, 1910, **43**, 2286.

[14] Riesenfeld, *Ber.*, 1905, **38**, 3380.

angles subtended by the pairs of oxygen atoms are only about 46°. The capacity of the transition metals of Groups IV, V, and VI, in their higher oxidation states, for forming peroxy-compounds can thus be ascribed to the ability of these elements to provide d^4sp^3 or d^3sp^3 hybrid orbitals,[15] giving valency angles sufficiently small to enable overlap with σ-bonding electron pairs donated by each of the oxygen atoms of a peroxy-ligand. This makes understandable both the preference for high co-ordination numbers and the frequent co-ordination of peroxy-groups in pairs. Where direct comparison is possible the thermal stabilities of peroxy-complexes in which the metal can provide these hybrids are higher than are those of compounds in which the metal has a lower co-ordination number and is using less favourable hybrid orbitals. For example, the CrO_5 adducts with bidentate ligands are thermally more stable than the pyridine complex.

Thermal stabilities of the tetraperoxy-salts of Group V elements[16] increase with increasing atomic number. Influence of increasing atomic size in relieving steric interference is to be expected, but the greater thermal stability and higher infrared frequency of tetraperoxychromates than of tetraperoxyvanadates show the limitations of this generalisation (since the covalent radii of vanadium and chromium are 1·22 and 1·17 Å, respectively).

EXPERIMENTAL

The less stable peroxy-compounds were prepared at $\not> 0°$, and were filtered off and washed without exposure to higher temperature. They were immediately pumped dry under a high-vacuum since most of the compounds are less stable in solution than in the crystalline state, and they were stored in the refrigerator. All measurements were made on freshly analysed samples. Methods for oxygen determination varied. "Total oxygen," O_T, determined iodometrically for chromium adducts or gasometrically[17] for the blue perchromates, includes oxidation equivalents from reduction to chromium(III). "Active oxygen," O_A, represents gas released on conversion of a peroxy-compound into the oxyanion of the metal. Specific measurement of peroxidic oxygen was made volumetrically (cf. Schwarz and Giese[10a]). Chromium was estimated by Wiede's method[6a] where applicable, but otherwise iodometrically. Molybdenum, tungsten, and vanadium were determined by standard methods after decomposition of the peroxide. Infrared spectra were recorded with a Perkin–Elmer 221 spectrophotometer over the range 5000—650 cm.$^{-1}$ for halogenocarbon and Nujol mulls. Magnetic susceptibilities were measured on the solids at 20°. Electrolytic conductivities were measured below room temperature when this was necessary to reduce decomposition.

Preparation of Tetraperoxy-salts.—The chromium,[17b] niobium, and tantalum[18] salts were prepared by established methods. To avoid contamination of ammonium tetraperoxychromate with triamminechromium tetroxide, it was necessary to filter off the salt without delay.

Potassium tetraperoxyvanadate was obtained by dropping a solution of the orthovanadate (2 g.) in 30% hydrogen peroxide (12 ml.) into a cold mixture of alcohol (25 ml.) and water (25 ml.) (Found: V, 17·3; O_A, 20·7. K_3VO_8 requires V, 17·2; O_A, 21·6%). The alternative procedure of running absolute alcohol into the solution, stated by Martinez and Rodriguez[4] to yield a different product, gave a less pure sample of the tetraperoxyvanadate, but one giving the same *X*-ray powder photograph. The crystalline salt is stable at 0° but is quickly decomposed in solution at this temperature. Ammonium tetraperoxyvanadate, prepared by Martinez and Rodriguez's method,[4] was of composition: NH_3, 21·7, 21·75; V, 21·7, 22·0; O_A, 27·3, 27·8% [Calc. for $(NH_4)_3VO_8$: NH_3, 21·9; V, 21·9; O_A, 27·5%]. The salt is stable in the cold for 7—10 days, but in solution decomposes even faster than the potassium salt.

Adducts from Chromium Diperoxide.—The triammine prepared according to Hofmann and Hiendlmaier's directions[6c] (O_T, 24·9%) was purified by heating it to 40° with 15% ammonia solution for 1 min. [Found: NH_3, 28·7; Cr, 30·8; O_T, 23·9. Calc. for $(NH_3)_3CrO_4$: NH_3, 30·5; Cr, 31·1; O_T, 23·9%]. A sample prepared completely by Riesenfeld's procedure,[6e] with

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[15] Duffey, *J. Chem. Phys.*, 1950, **18**, 943, 1444; Pauling, "Nature of the Chemical Bond," Oxford Univ. Press, 2nd edn., p. 108.

[16] Melikov and Jelchaninoff, *Ber.*, 1909, **42**, 2291.

[17] (*a*) Wiede, *Ber.*, 1898, **31**, 516; (*b*) Riesenfeld, Wohlers, and Kutsch, *Ber.*, 1905, **38**, 1885.

[18] Sieverts and Müller, *Z. anorg. Chem.*, 1928, **173**, 297.

the temperature raised to 40° for 3 min., was of similar purity (O_T, 24·1%). Decomposition of the compound in aqueous solution causes the conductivity to rise rapidly from the low initial value.

Ethylenediaminechromium diperoxide [6d] was of composition: C, 11·8; H, 5·8; N, 12·3; Cr, 23·6, 23·9; O_T, 18·6%; peroxy-groups per Cr, 1·90 (Calc. for $C_2H_8N_2CrO_4,2H_2O$: C, 11·3; H, 5·7; N, 13·2; Cr, 24·5; O_T, 18·9%). The compound is somewhat soluble in aqueous ammonia, but almost insoluble in water and organic solvents.

Adducts from Chromium Oxide Diperoxide.—Samples of the blue-violet pyridine complex as prepared (i) from aqueous solution [14] and (ii) from ether,[19] gave the same infrared spectrum, magnetic susceptibility, and electrolytic conductivity [Found: (i) C, 29·2; H, 2·7; N, 6·9; Cr, 24·6; (ii) C, 27·9; H, 3·0; N, 6·5; Cr, 24·65. Calc. for $C_5H_5NCrO_5$: C, 28·4; H, 2·4; N, 6·6; Cr, 24·65%]. In our experience some preparations obtained by the latter method are liable to be less stable than those from the former, sometimes detonating spontaneously at ordinary temperature. The compound is insoluble in water, but dissolves in organic solvents.

The 2,2′-bipyridyl adduct was obtained by adding a solution of the base (0·5 g.) in ether to the ethereal peroxide solution from chromic acid (1·0 g.). The blue *complex* was precipitated immediately (Found: C, 41·7; H, 2·7; N, 9·7; Cr, 18·05; O_T, 19·2. $C_{10}H_8N_2CrO_5$ requires C, 41·6; H, 2·8; N, 9·7; Cr, 18·05; O_T, 19·4%). It reacts quickly with acidified potassium iodide, but not readily enough with permanganate to permit direct determination of peroxy-groups. It is readily soluble only in dimethylformamide and pyridine amongst common solvents. Heated alone, the compound decomposes quietly at 120—140°.

The 1,10-phenanthroline complex [20] was prepared similarly (Found: C, 45·6; H, 2·6; N, 8·7; Cr, 16·8, 16·9. Calc. for $C_{12}H_8N_2CrO_5$: C, 46·2; H, 3·2; N, 9·0; Cr, 16·7%). Properties of this compound, which explodes at 120°, are otherwise similar to those of the bipyridyl complex.

Blue Ammonium Perchromate.—A solution of ammonium chloride (10 g.), ammonium dichromate (2 g.), and acetic acid (5 ml.) in water (100 ml.) was cooled to −10°. 30% Hydrogen peroxide solution (5 ml.) was added dropwise with stirring, so that the temperature did not rise above −6°. The precipitate was immediately collected and washed with small portions of water, alcohol, and ether. It was pumped free from solvent under a high vacuum, this taking preferably not more than 30 min. (yield 1·2 g.) [Found: Cr, 27·8; O_T, 34·9%; peroxy-groups per Cr, 2·41. Calc. for $(NH_4)_2Cr_2O_{12},2H_2O$: Cr, 28·1; O_T, 34·8%; peroxy-groups, 2·5]. At room temperature the salt decomposes completely to ammonium dichromate in a few days. From 0·2701 g., permanent gas (0·0604 g.) and water (0·0243 g.) were produced (Calc.: O_2, 0·0587 g.; H_2O, 0·0264 g.). No hydrogen peroxide can be pumped from the freshly prepared salt under a high vacuum (cf. ref. 17*a*).

In an attempt to prepare the blue perchromate of cæsium the supposed compound was precipitated by addition of alcohol, but it detonated when an attempt was made to remove it from the filter.

Potassium Hydrogen Diperoxymolybdate and Tungstate.—For the preparation of potassium hydrogen diperoxytungstate [11] a solution containing potassium tungstate (2 g. in 20 ml. of water) and 30% hydrogen peroxide solution (4 ml.) was acidified with sufficient 8N-nitric acid (1—2 ml.) to discharge the yellow colour. The salt was obtained by evaporation in a vacuum [Found: K (by flame photometry), 11·1; W, 52·2; O_A, 9·3. Calc. for $KHWO_6,2H_2O$: K, 11·0;

TABLE 2.

d Values for *X*-ray powder lines from tetraperoxy-salts.

K_3VO_8	K_3CrO_8	$(NH_4)_3VO_8$	$(NH_4)_3CrO_8$	K_3VO_8	K_3CrO_8	$(NH_4)_3VO_8$	$(NH_4)_3CrO_8$
5·04m	5·04s	5·30s	5·28s	1·85s	1·85s	1·94w	1·94m
4·72w	4·70w	4·93s	4·93s	1·80w	1·81m	1·88w	1·89m
3·34m	3·34m	3·49w	3·51w	1·68m	1·68m, 1·66m		
2·98s	2·97s	3·13s	3·12s	1·50s	1·50m, 1·49m	1·57w	1·56m
2·78m	2·79m	2·92m	2·92m	1·47m	1·46m	1·52w	1·52m
2·36s	2·36s	2·46m	2·47s	1·37m	1·38m	1·43m	1·43m
2·02w	2·03w	2·11w	2·11m	1·25m	1·25m	1·30m	1·30m
1·93m	1·91m	2·05w	2·05w	1·19m	1·19$_3$m, 1·18$_7$m		1·24m

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[19] Schwarz and Giese, *Ber.*, 1932, **65**, 871.
[20] Evans, *J.*, 1957, 4013.

W, 51·7; O_A, 9·0%]. The molybdenum salt was prepared similarly (colour change, red to yellow), but was precipitated by addition of alcohol (Found: K, 16·0; Mo, 35·6; O_A, 12·0. Calc. for $KHMoO_6,2H_2O$: K, 14·6; Mo, 35·8; O_A, 11·9%). The complicated *X*-ray powder patterns were not so similar as to place isomorphism of the salts beyond doubt.

X-*Ray Powder Data.*—The spacings of the powder lines from tetraperoxyvanadate and chromate with the same cation are almost identical (Table 2). Likewise, isomorphism of ammonium and potassium salts is shown by the proportionate *d* values of corresponding lines.

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