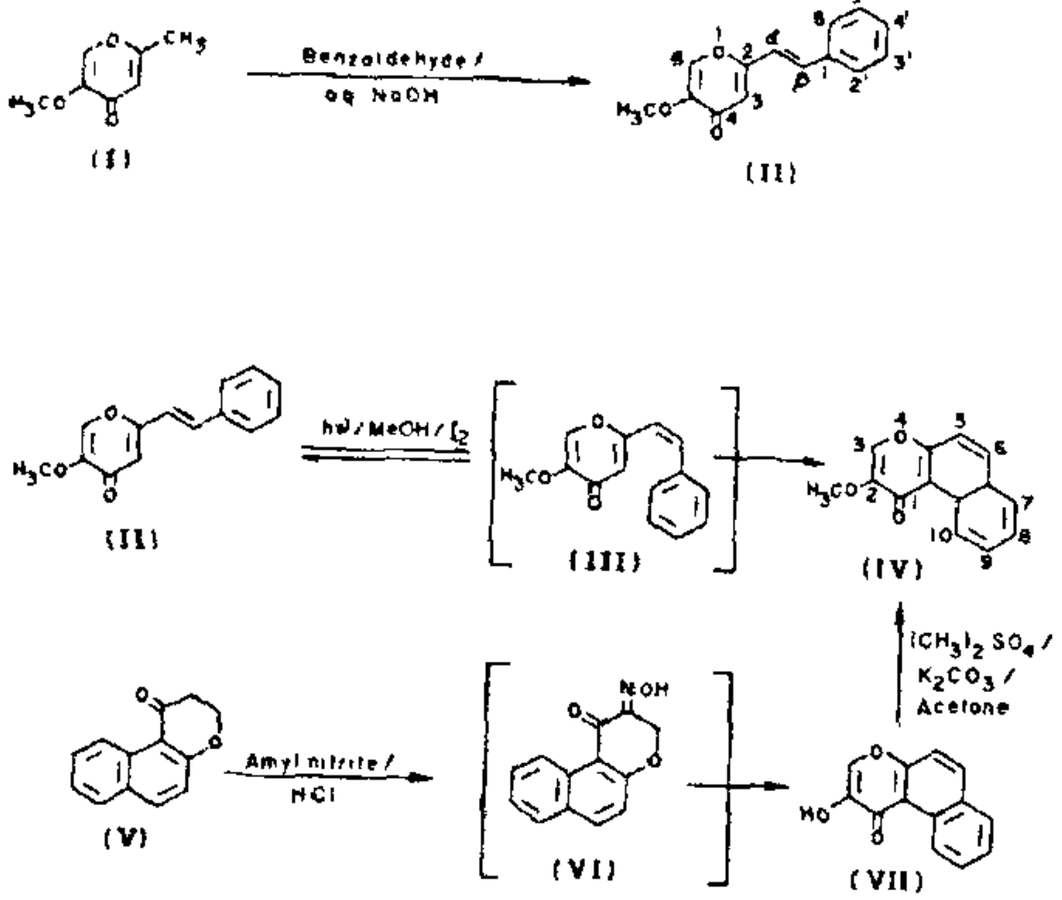

(*i*) *Synthesis of 2-hydroxy-1H-naphtho[2,1-2b]pyran-1-one* (VII). A solution of benzo(f) chromanone (V)[3] (6 g) in methanol (40 ml) was kept in an ice chest and small quantities of amylnitrite (18 g) and conc. hydrochloric acid (36 ml) were alternately added with shaking. The resulting solution gradually turned up red and after complete addition the reaction mixture was gently heated on a flame for 2 hr. The reaction mixture was poured into ice (100 g) whereupon a brown yellow solid was precipitated. It was filtered and crystallised from methanol as yellow flakes (3 g, 48%); m.p. 130–32° (Found: C, 73.60; H, 3.74 calculated for $C_{13}H_8O_3$ C, 73.58; H, 3.77%). $M^{+\cdot}$ m/e 212.

(*ii*) *2-Methoxy-1H-naphtho[2,1-b]pyran-1-one* (*IV*)

A mixture of 2-hydroxy-1H-naphtho[2,1-b]pyran-1-one (VII) (1 g), dimethyl sulphate (0.7 ml), potassium carbonate (10 g) and acetone (150 ml) was refluxed for 10 hr. The solution was distilled to remove acetone and crushed ice added to the residue. The brown semi-solid, that separated, crystallized from methanol as brown needles of 2-methoxy-1H-naphtho[2,1-b]pyran-1-one (IV) (0.97 g, 90%), m.p. 40° The photoproduct (IV) was found to be identical in all respects (mp, mmp and superimposable i.r.) with the authentic sample of 2-methoxy-1H-naphtho [2,1-b] pyran-1-one.

8 February 1982

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X-RAY SPECTROSCOPIC DETERMINATION OF THE VALENCE STRUCTURE OF THE SPINEL $NiMnCrO_4$

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ALTHOUGH some information about the spinel $NiMnCrO_4$ is available[1], it was thought worthwhile to study the spinel x-ray spectroscopically, to determine its valence structure uniquely. The compound $NiMnCrO_4$ was prepared by the oxide method[2] and the formation was confirmed by the x-ray powder method. The observed $1/d^2$ values for various reflections along with the calculated $1/d^2$ values and observed and calculated intensities of the various diffraction lines are given in table 1. The x-ray spectroscopic results for manganese and chromium ions are given in table 2 and 3 respectively. The detailed procedure for calculation of intensities and x-ray spectroscopic determination of oxidation states of cations have already been reported[3].

TABLE 1

X-ray diffraction data of the spinel $NiMnCrO_4$

hkl	I/d^2		Intensity	
	Obs.	Cal.	Obs.	Cal.
111	0.0447	0.0438	10	5.3
220	0.1178	0.1169	25	24.7
311	0.1604	0.1604	100	100
222	0.1788	0.1754	10	8.8
400	0.2372	0.2339	25	22.4
422	0.3530	0.3510	10	9.5
511	0.3940	0.3949	30	24.5
440	0.4666	0.4678	50	52.3
533	0.6329	0.6434	10	10.5
731	0.8510	0.8528	15	14.3
751 555	1.0796	1.0950	<5	5.8 1.9
844	1.3859	1.4016	30	31.6
951	1.5453	1.5622	20	18.5

$a = 8.28 \pm 0.02$ A°

The possible valence structures for this spinel are

(i) $Ni^{+2}Mn^{+3}Cr^{+3}O_4^{-2}$ (ii) $Ni^{+2}Mn^{+4}Cr^{+2}O_4^{-2}$

(iii) $Ni^{+3}Mn^{+2}Cr^{+3}O_4^{-2}$ (iv) $Ni^{+3}Mn^{+3}Cr^{+2}O_4^{-2}$

TABLE 2

Data on K absorption edges of manganese

Absorber	Valency	Wavelength	$\Delta\lambda$ (X.u).	ΔE(eV)
Mn metal (Cauchois and Hulubei)[6]	—	1892.54	—	—
Mn metal (present work)	—	1892.60	—	—
MnO	2	1890.8	1.8	6.2
Mn_2O_3	3	1888.9	3.7	12.5
MnO_2	4	1887.6	5.0	17.3
$NiMnCrO_4$	—	1890.9	1.7	5.9

TABLE 3

Data on K absorption edges of chromium

Absorber	Valency	Wavelength	$\Delta\lambda$ (X.u).	ΔE(eV)
Cr metal (Cauchois and Hulubei)[6]	—	2065.95	—	—
Cr Metal (present work)	—	2066.1	—	—
$Cr(CO_3)$	2	2064.8	1.3	3.7
$Cr(CH_3COO)_2$	2	2064.6	1.5	4.3
Cr_2O_3	3	2063.4	2.7	7.9
$Cr_2(SO_4)_3$	3	2063.2	2.9	8.4
$NiMnCrO_4$	—	2063.5	2.6	7.6

From tables 2 and 3 it is seen that manganese and chromium ions exist in divalent and trivalent states respectively. However x-ray crystallographic results[1] show that manganese ions are in the trivalent state and occupy the tetrahedral site. It might be mentioned that the observed cubic symmetry of the spinel, rules out the presence of the distorting Mn^{+3} ions giving support to our result. Thus the valence structure of this spinel is $Ni^{+3}Mn^{+2}Cr^{+3}O_4^{-2}$

From the intensity ratios I_{220}/I_{422} and I_{422}/I_{400}, it is seen that Mn^{+2} ions occupy the tetrahedral sites. The site preference energies[4] also support the result as it is seen that Mn^{+2} ions have a larger preference for the tetrahedral sites than the remaining two ions namely Ni^{+3} and Cr^{+3}. The lattice parameter calculated empirically[5] show the best match for Mn^{+2} ions occupying tetrahedral sites. Hence we may write the ionic structure of this spinel as

$$Mn^{+2}\ [Ni^{+3}Cr^{+3}]\ O_4^{-2}$$

4 July 1981

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