

## Photolysis of water absorbed by photosensitive sodium sulphide during solid state interaction with $V^{2+}$ , $Cr^{2+}$ and $Mn^{2+}$ ions in sun light

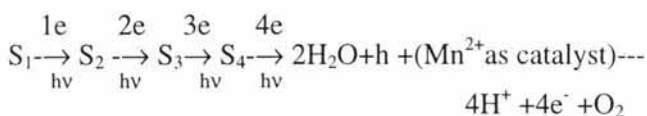
Lakshmi\*, A Sahay, S Shukla<sup>†</sup> & S Singh<sup>‡</sup>

Department of chemistry, D.D.U.Gorakhpur University,  
 Gorakhpur, 273 009, India

Received 7 February 2000; revised 4 September 2000

Sulphides of transition metal ions ( $M^{2+}=V^{2+}$ ,  $Cr^{2+}$  and  $Mn^{2+}$ ) in solid state have been synthesised by reaction with  $Na_2S.7H_2O$  in the presence of sunlight. XRD patterns show that these compounds are not  $M_xS_y$  but mercaptyl hydroxyl metal sulphides,  $[M(SH)(OH)(H_2O)_2]$ . Structure is further ascertained by IR spectra showing bands due to  $T_d$ -symmetry. The presence of hydroxyl, mercaptyl and aqua groups has been confirmed with TGA, DTA and ESCA.

Bassel Kok<sup>1</sup> suggested that electron generation complex in photosystem II exists in several transient states of oxidation called S states where each S state contributed to a four stage water oxidation cycle or clock. After each flash of light ( $1h\nu$ ) S clock operates and yields four electrons.



The clock then removes 4 electrons from water molecules in the presence of sunlight. It is reported<sup>1</sup> that protein bound to manganese is believed to catalyse electron transfer reaction during photosynthesis. Similarly photosensitive<sup>2-4</sup>  $Na_2S.7H_2O$  has 7 bound water molecules and may have

capacity to produce 14 electrons in the presence of a catalyst ( $V^{5+}$  or  $Cr^{6+}$  or  $Mn^{7+}$ )<sup>5-9</sup>. Thus reduction of  $Mn^{7+} + 5e \rightarrow Mn^{2+}$  can easily take place forming  $[Mn(SH)(OH)(H_2O)_2]$ , an unusual complex. Similarly reduction,  $Cr^{6+} + 4e \rightarrow Cr^{2+}$  and  $V^{5+} + 3e \rightarrow V^{2+}$  will take place during solid - state interaction of reactants in the presence of sun-light ( $h\nu$ ).

### Experimental

Sodium sulphide ( $Na_2S.7H_2O$ ), purity 99.97% Emerk, ammonium meta vanadate ( $NH_4VO_3$ ) purity 99.99%, (BDH) potassium dichromate, purity 99.8%, (Emerk) and potassium permanganate purity 99.98%, (BDH), were used for preparing the final product. 1:1 Molar ratio mixture of  $Na_2S.7H_2O$  and reactants were interacted in sun light for 45 minutes. There was rise in temperature as shown in Table 1. Current and voltage were measured as shown in Table 2.

The final products  $[M(SH)(OH)(H_2O)_2]$ , were purified through vigorous washing with distilled water for several times. The final washing was completed with removal of  $S^{2-}$  ion.

The elemental analysis was carried out with the help of ESCA, results are given as follows. For  $KMnO_4$  reaction the product obtained  $[Mn(SH)(OH)(H_2O)_2]$  was brownish black, mol. wt. 141.161,  $\mu_s = 5.91$  BM, Calc: H, 8.16; O, 30.16; S, 22.74; and Mn, 38.96%; Obs H, 8.10; O, 30.21; S, 22.69; and Mn, 38.87%.

For  $K_2Cr_2O_7$  reaction the product obtained  $[Cr(SH)(OH)(H_2O)_2]$  was greenish blue, mol wt. 138.061,  $\mu_s = 4.03$  BM, Calc. H, 9.01; O, 30.31; S, 23.02; and Cr, 37.66%; Obs. H, 9.12; O, 30.21; S, 23.05, and Cr, 37.59%

For  $NH_4VO_3$  reaction the product obtained  $[V(SH)(OH)(H_2O)_2]$  was blackish brown mol wt. 137.168,  $\mu_s = 3.05$  BM, Calc. H, 10.02; O, 30.58; S, 23.35; and V, 37.14%; Obs. H, 10.18; O, 30.68; S, 23.25; and V, 37.10%

<sup>†</sup> University Service Instrumentation Center, Delhi University, Delhi 110 007

<sup>‡</sup> Project Fellow, UGC, New Delhi 110 007

Table 1 — Rise in temperature during solid state reaction in the presence of sun light

KMnO<sub>4</sub> + Na<sub>2</sub>S. 7 H<sub>2</sub>O System ↓

Time (min.)	Temp °C
3.05 (PM)	25
3.10	30
3.15	36
3.20	38
3.25	39
3.30	43
3.85	48
3.40	44
3.50	31
3.55	25

K<sub>2</sub>Cr<sub>2</sub>O<sub>7</sub> + Na<sub>2</sub>S. 7H<sub>2</sub>O ↓↓

Time (min.)	Temp °C
2.35 (PM)	24
2.40	30
2.45	34
2.50	25
2.53	22

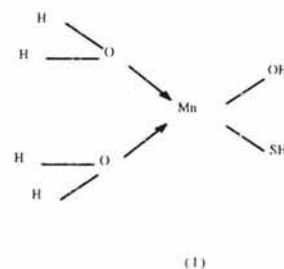
NH<sub>4</sub>VO<sub>3</sub> + Na<sub>2</sub>S. 7 H<sub>2</sub>O ↓

Time (min.)	Temp °C
1.50	25
1.55	30
2.00	35
2.05	32
2.10	28
2.15	25

↓ [KMnO<sub>4</sub>] = 1.581 g ; ↓↓ [K<sub>2</sub>Cr<sub>2</sub>O<sub>7</sub>] = 2.159 g ; ↓ [NH<sub>4</sub>VO<sub>3</sub>] = 1.607 g ; [Na<sub>2</sub>S.7H<sub>2</sub>O] = 2.014 g ; RT = 20<sup>0</sup>C ; ST = 25<sup>0</sup>C ;

## Results and discussion

Sodium sulphide is photosensitive<sup>1,2</sup> and hygroscopic in nature. In the present investigation two new products of sodium sulphide [Na(SH)(H<sub>2</sub>O)<sub>3</sub>] and [Na(OH)(H<sub>2</sub>O)<sub>3</sub>] tetrahedral structure of which have been ascertained by IR (ν SH, νOH and δ OH<sub>2</sub>



(1)

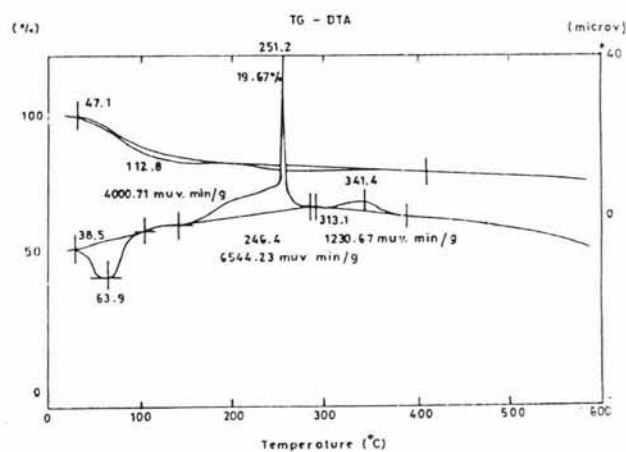


Fig. 1 — TG-DTA of compound of Mn(II)

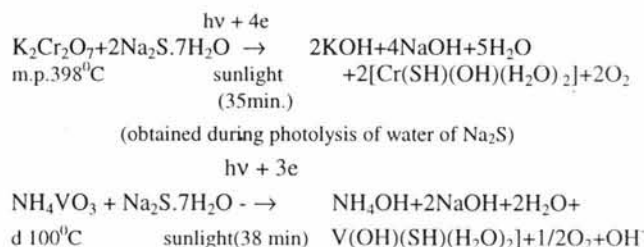
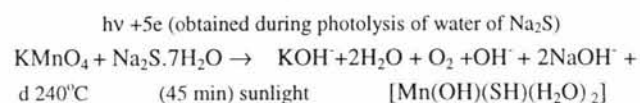
at 2353 cm<sup>-1</sup>, 2071 cm<sup>-1</sup> and 1635 cm<sup>-1</sup> respectively with bands of T<sub>d</sub> symmetry) have been obtained. Two new strong lines do appear in XRD pattern (d = 2.617 Å<sup>0</sup>(I/I<sub>0</sub> = 100) d = 2.629 Å<sup>0</sup>(I/I<sub>0</sub> = 94)) (Table 3). This water absorbing tendency of sodium sulphide shows a rise in temperature by 8<sup>0</sup>C in the presence of sunlight. Thus light energy absorbed by sodium sulphide during absorption of water molecules is converted to heat energy and electrical energy as well (Table 1 and Table 2). When sodium sulphide interacted with KMnO<sub>4</sub>, K<sub>2</sub>Cr<sub>2</sub>O<sub>7</sub> and NH<sub>4</sub>VO<sub>3</sub>, [Mn<sup>+7</sup>, Cr<sup>+6</sup> and V<sup>+5</sup> oxidation state] showed rise in temperature by 20<sup>0</sup>C and rise in voltage and current. Products of brownish black, greenish blue, and blackish brown colour were obtained respectively. The IR spectra of the products showed bands of T<sub>d</sub> symmetry and νSH, νOH, νHOH modes of vibrations suggesting structure I.

Thus oxidation state of Mn is reduced to Mn<sup>+2</sup> from Mn<sup>+7</sup> by capturing 5 electrons (Mn<sup>+2</sup>, d<sup>5</sup>, system). Similarly the other reduction processes occur; Cr<sup>+6</sup> + 4e → Cr<sup>+2</sup> (d<sup>4</sup> system) and V<sup>+5</sup> + 3e → V<sup>+2</sup> (d<sup>3</sup> system). These oxidation states have been ascertained with μ<sub>s</sub> values. These points ascertain the

Table 2- Rise in current and voltage

NH <sub>4</sub> VO <sub>3</sub> + Na <sub>2</sub> S. 7H <sub>2</sub> O			K <sub>2</sub> Cr <sub>2</sub> O <sub>7</sub> + Na <sub>2</sub> S. 7H <sub>2</sub> O		
Time (min.)	mV	mA	Time (min.)	mV	mA
1.5 (PM)	160	5.3	1.00	182	8.3
2.0	170	5.7	1.15	340	7.9
2.1	190	7.2	1.30	390	8.4
2.2	244	7.7	1.45	389	8.9
2.3	154	7.0	2.00	224	10.2
2.4	164	6.5	1.15	246	11.2
2.5	204	5.7	2.30	224	13.2
3.0	240	5.3	2.45	210	7.5
3.1	240	5.3	3.00	191	7.8
KMnO <sub>4</sub> + Na <sub>2</sub> S. 7 H <sub>2</sub> O			Na <sub>2</sub> S (s)		
Time (min.)	mV	mA	Time (min.)	mV	mA
1.25	125	7.0	1.40	1.91	7.1
1.35	212	11.4	1.50	204	7.2
1.45	370	19.1	2.00	204	7.3
1.55	442	20.9	2.10	200	7.1
2.05	568	26.3	2.20	191	7.0
2.15	572	25.9	2.30	184	7.0
2.25	544	26			
2.35	621	28			
2.45	541	28			

possibility of photolysis of water molecules which were absorbed by hygroscopic, photosensitive<sup>1,2</sup> sodium sulphide from atmosphere in the presence of sun light only. Thus Na<sub>2</sub>S.7H<sub>2</sub>O absorbs extra water molecules which decomposes in following way causing photolysis<sup>1</sup> of water 2H<sub>2</sub>O (Mn<sup>+2</sup> as catalyst) → 4H<sup>+</sup> + 4e + O<sub>2</sub>. These electrons in turn reduce (Mn<sup>+7</sup> + 5e → Mn<sup>+2</sup>) the reactions may be written as follows.



Thus due to photolysis of atmospheric H<sub>2</sub>O molecule first reduction of transition metal ion takes place which on account of availability of vacant *d*-orbitals in transition metal ion attracts donor

Table 3 — XRD Pattern of the final products and sodium sulphide

I/10	100	90	75	60	Products
d (Å)	3.851	4.054	3.061	—	[Mn(SH)(OH)(H <sub>2</sub> O) <sub>2</sub> ]
d (Å)	3.242	—	2.993	—	[Cr(SH)(OH)(H <sub>2</sub> O) <sub>2</sub> ]
d (Å)	2.891	2.871	3.846	3.92	[V(SH)(OH)(H <sub>2</sub> O) <sub>2</sub> ]
d (Å)	2.617	—	5.988	2.749	[Na(SH)(H <sub>2</sub> O) <sub>3</sub> ]
	2.629(97)	—	—	—	[Na(OH)(H <sub>2</sub> O) <sub>3</sub> ]

Table 4 — TGA of the solid state compounds Mn(SH)(OH)(H<sub>2</sub>O)<sub>2</sub>

Weight Loss (%)	Temp. (°C)	(1/K)(E <sub>3</sub> )	
2.00	45.48	2.1397	
4.00	57.43	3.0255	
6.00	69.20	2.9214	
8.00	79.59	2.8354	
10.00	89.85	2.7552	
12.00	106.78	2.6324	(-H <sub>2</sub> O)
14.00	184.92	2.4509	
16.00	178.00	2.2168	
18.00	225.87	2.0061	(-SH, OH)
20.00	425.59	1.4313	(-2H <sub>2</sub> O)
22.00	562.82	1.1970	
			[Cr(SH)(OH)(H <sub>2</sub> O) <sub>2</sub> ]
5.00	110.00	2.6103	(-H <sub>2</sub> O)
10.00	117.95	2.2171	
15.00	215.90	2.0450	
20.00	244.50	1.9320	(-OH)
25.00	294.25	1.7626	
30.00	376.40	1.5397	(-SH)
35.00	440.00	1.4023	
40.00	499.30	1.2947	(-2 H <sub>2</sub> O)
			[V(SH)(OH)(H <sub>2</sub> O) <sub>2</sub> ]
5.00	41.39	3.1797	
10.00	61.64	2.9874	
15.00	91.27	2.7445	(-H <sub>2</sub> O)
20.00	122.84	2.5256	
25.00	214.38	2.0514	(-SH)
30.00	236.65	1.9617	(-OH)
35.00	258.65	1.8806	(-2H <sub>2</sub> O)

molecules and forms mercaptyl hydroxyl complexes instead of sulphide M<sub>x</sub>Sy<sup>10</sup>

[Mn(SH)(OH)(H<sub>2</sub>O)<sub>2</sub>] compound shows bands at 3896, 3834, 3718, 3708, 3647 cm<sup>-1</sup> 3400 cm<sup>-1</sup> due to ν OH(H<sub>2</sub>O) and a band at 2360 cm<sup>-1</sup> due to ν SH modes of vibration. Bands at 1643, 1538 are due to δ SH δ OH bending modes of vibrations along with T<sub>d</sub> symmetry bands at 1102, 773 and 618 cm<sup>-1</sup>. The metal-sulphur stretching frequency occurs at 514 cm<sup>-1</sup> showing metal ion (Mn<sup>2+</sup>, d<sup>5</sup>) in coordination sphere with a magnetic moment 5.91 B.M. The bands at 2360 cm<sup>-1</sup> (νSH) and 2059 cm<sup>-1</sup> (OH) are absent in compounds of Zn<sup>2+</sup>, Cd<sup>2+</sup> and Hg<sup>2+</sup> ions because of completely filled (nd<sup>10</sup> system). The bands at 3734, 3460, 3400 cm<sup>-1</sup> are due to presence of water molecules. The I.R. bands at 2360 and 2042 cm<sup>-1</sup> are due to (νSH and νOH) respectively. The band at 1633 cm<sup>-1</sup> is due to δ HOH. The bands at 1227, 918, 764, are due to T<sub>d</sub> symmetry. The bands at 669 and 501 cm<sup>-1</sup> are due to ν Cr-O and ν Cr-S respectively with a value of magnetic moment 4.03 B.M.

In solid compound [V(SH)(OH)(H<sub>2</sub>O)<sub>2</sub>] the bands at 3430 and 3200 cm<sup>-1</sup> are due to ν H<sub>2</sub>O symmetric and asymmetric modes of vibrations respectively. The bands<sup>10</sup> at 2360, 2043 cm<sup>-1</sup> are due to νSH and νOH respectively.

δ HOH is very weak and appears at 1600 cm<sup>-1</sup>. The bands at 1216, 966, 763 cm<sup>-1</sup> are due to T<sub>d</sub> symmetry. Finally the bands at 670, 515 cm<sup>-1</sup> are due to νV - O and νV - S respectively with a magnetic moment 3.05 B.M.

The compound obtained during solid state interaction of Na<sub>2</sub>S.7H<sub>2</sub>O and KMnO<sub>4</sub> in presence of sun-light shows an endotherm at 63.9°C with ΔH value 4000.71 muv. (mass unit volt) min/g (Fig. 1 Table 4, 5) with a mass loss of 19.57% due to water molecules outside the coordination sphere. An

Table 5 — DTA-exotherm and endotherm of the compounds

[Mn(SH)(OH)(H <sub>2</sub> O) <sub>2</sub> ]	
Compound prepared in Solid-State	
Exotherm	351.2, 341.4(°C)
-ΔH (muv.min/g)	6544.23, 1230.67
Endotherm	63.9 (°C)
+ΔH (muv.min/g)	4000.71
[Cr(SH)(OH)(H <sub>2</sub> O) <sub>2</sub> ]	
Compound prepared in solid-state	
Exotherm	201.2, 484.7(°C)
-ΔH (muv.min/g)	346.56, 3941.21
Endotherm	90.5 (°C)
+ΔH (muv.min/g)	411.88
[V(SH)(OH)(H <sub>2</sub> O) <sub>2</sub> ]	
Compound prepared in solid-state	
Exotherm	290.1, 445.6(°C)
-ΔH (muv.min/g)	1826.65, 1537.3
Endotherm	114.9, 110.2(°C)
+ΔH (muv.min/g)	7418.0

exotherm at 251.2 is due to escape of SH and OH group with ΔH value 6544.23 muv.min/g. Further an exotherm at 341.4 occurs due to escape of water molecule from coordination sphere with ΔH value 1230.67 muv.min/g. Thermal stability of the compound is up to 250°C.

The solid compound [Cr(SH)(OH)(H<sub>2</sub>O)<sub>2</sub>] shows endotherms at 90.5 and 110 °C with ΔH 4113.88 muv.min/g due to water molecules outside the coordination sphere. The compound shows gradual mass loss of 41.037% due to escape of SH and OH groups ( Table 4a). Finally there is an exotherm at 484.7 °C with ΔH value 3941.21

muv.min/g showing the escape of water molecules from coordination sphere. Thermal stability of the compound is up to 244°C.

The solid compound [V(SH)(OH)(H<sub>2</sub>O)<sub>2</sub>] shows endotherms at 114.9, 110.2 °C with a ΔH value 7418.0 muv.min/g due to water molecules outside the coordination sphere. There is an exotherm at 290.1 °C with ΔH value . 1826.65 muv.min/g (Table 5) showing the escape of SH, OH groups from the coordination sphere. Finally there is an exotherm at 445.6 °C ΔH 1537.3 muv.min/g due to escape of water molecules from the coordination sphere. Thermal stability of the compound is up to 290°C.

### Acknowledgement

Authors are thankful to UGC New Delhi for financial assistance(Grant No.F12-3/98(SR-1))for this work.

### References

- 1 Kok B & Srivastava H S, in *Plant Physiology*, ( Rastogi Publications, India).178 1999.
- 2 Mellor, J W. *Comprehensive Treatise on Inorganic theoretical chemistry*, Vol.2 Supplement Na, Li, 981-82, (Longmans Green . New York) 1961.
- 3 Dhar N R & Raghvan B Y S, *Proc Nat Acad Sci , India* . 17 A (1948) 7.
- 4 Huheey J E , *Inorganic chemistry* (Harper collins) ( 1995) 915
- 5 Cotton F A & Wilkinson G, *Advance inorganic chemistry*, (Willey Eastern , New Delhi) 1998
- 6 Adams D M & Arnold E, *Metal ligand and related vibration*,( London) 1967.
- 7 Ardan A& Taube H, *J Am chem. Soc.*,89 (1967) 3661.
- 8 Worth B C, Demetsion B & Grazescowisk R, *Trans met chem*, 4 (1979) 187.
- 9 Nakamoto K, Fugita J& Kabayashi, *J Am chem Soc*, 74 (1957).4904
- 10 Mishra J P & Lakshmi , *J Solid state Chem*, 45 (1982).381.