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Spectroscopic Studies and Structural Chemistry of Cr^{III}/Cr^{VI} Compounds in the Solid State

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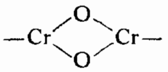
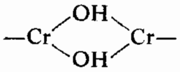
Received March 25, 1968

In this paper the studies on the structure and properties of brown products formed in Cr^{III} and Cr^{VI}—containing solutions are presented. On the basis of thermogravimetric, spectroscopic (reflection and absorption spectra in the UV, visible and IR region) and magnetic (Gouy method) and electronic paramagnetic resonance (EPR) studies the conclusions were drawn. The original products were found to be a mixture of complex compounds with the structure:





Above 166°C these compounds are converted to form new mono-bridged structures: –Cr–O–Cr–, –Cr–OH–Cr–. Above 200°C these products decompose with a simultaneous reduction of chromium(VI) to chromium(III) and a partial disproportionation $Cr^{III}+Cr^{VI}=Cr^{IV}$. As a final decomposition product the mixture Cr_2O_3 (about 92%) $+CrO_2$ (about 8%) is obtained. An extensive discussion of the results follows. The reflection and absorption spectra enabled us to calculate the crystal field parameters Δ and the Racah B coefficients. The vibrations of the definite function groups have been assigned to the particular infrared bands.

Introduction

The problem of the simultaneous occurrence of both Cr^{III} and Cr^{VI} in aqueous solutions[1,2,3] as well as the mixed compounds formed, has been, until now, extensively studied. The simultaneous occurrence, of both these oxidation states of chromium in solid phase has not, until now, been definitely established. Earlier works[4,5,6] dealing with the subject were rather of a preparative character and did not make clear the structure and properties of Cr^{III}–Cr^{VI} compounds. This problem has been more thoroughly studied by Bhatnagar,[7,8] Cameron[9] and co-workers who were dealing with the magnetic properties of brown products formed in solutions containing both the CrO_4^{2-} and Cr^{3+} ions. It is, however, significant that no literature concerning the spectroscopic properties of these compounds is available. We hope that our studies on the magnetic and spectroscopic properties of the Cr^{III}–Cr^{IV} compounds will provide some new evidence for the elucidation of the structure and the properties of these compounds.

Experimental Section

Preparative Work. The Cr^{3+} ions react at pH = 4.6-5.6 with the CrO_4^{2-} ions, giving a brown precipitate which is in many respects similar to $Cr(OH)_3$ because of its colloidal consistency, constant changing of water percentage and ageing. The product has been obtained by the methods listed below:

(1) Bhatnagar's method,[7,8] by the reaction of $Cr(OH)_3$ suspension with 5% solution of chromic acid;

(2) Dunnicliff's method,[4] by the addition of chromic acid to the $Cr_2(SO_4)_3$ solution;

(3) by the addition of ammonia potassium chromate solution to aqueous chromium nitrate;

(4) by the direct reactions of Cr^{3+} with CrO_4^{2-} and filtration of the precipitated chromite;

(5) by the gamma irradiation of ammonium dichromate solutions over the concentration range 10^{-5}-1 *M* with a dose pf 1.37×10^{23} eV.[10]

The colloidal products became fine crystalline after a few day ageing; in such form they were filtered, thoroughly washed from the absorbed ions and dried *in vacuo*. It was found that the products obtained by these methods have the same magnetic and spectroscopic properties, so that they are the same compounds. Quantitative analysis has shown that this compound has a definite $Cr^{III}:Cr^{VI}$ ratio, equal to 2:1. It differs from the complex formed in the aqueous solutions of

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(1) H. L. Krauss and G. Gnatz, *Chem. Ber.*, 92, 2110 (1959).
(2) E. L. King and J. A. Neptune, *J. Am. Chem. Soc.*, 77, 3186 (1955).
(3) A. H. W. Alen, H. Steinberg, and D. Heyman, *Recusil Trav. Chim. Pays Bas*, 72, 94 (1953).
(4) H. B. Dunnicliff and G. S. Kowani, *J. Phys. Chem.*, 35, 3214 (1931).
(5) D. S. Datar and S. K. K. Jatkar, *J. Indian. Inst. Sci.*, 22A, 309 (1939).
(6) P. C. R. Chandhurry, *J. Ind. Chem. Soc.*, 16, 652 (1939).
(7) S. S. Bhatnagar, B. Prakash, and A. Hamid, *J. Chem. Soc.*, 1428 (1938).
(8) S. S. Bhatnagar and J. Mittarb, *J. Chem. Soc.*, 1433 (1939).
(9) A. Cameron, E. H. Harbard, and A. King, *J. Chem. Soc.*, 55 (1939).
(10) J. Nawojska, *Ann. Soc. Chim. Polonorum*, 41, 889 (1967).

formula $[Cr(OH)_2^+][HCrO_4^-]$ and 1:1 ratio which was found by Krauss and Gnatz.[1]

Thermogravimetric Studies. The original product was subjected to thermogravimetric analysis by heating to 500°C. The results are shown in Figure 1 as a differential curve $\Delta G/G=f(t)$.

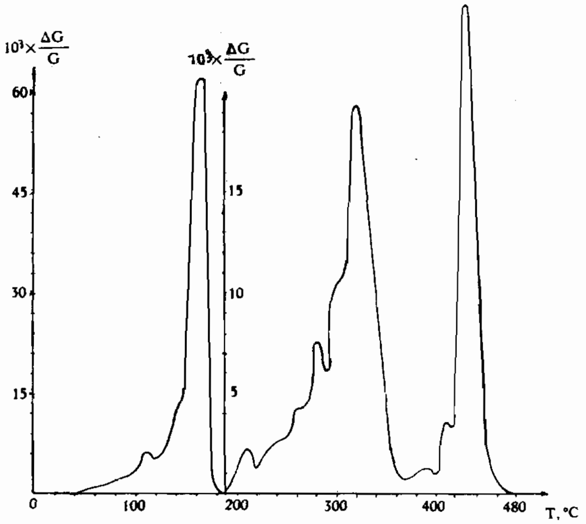

Figure 1. Differential curve $\frac{\Delta G}{G}=f(T)$.

There are three maxima at 166°, 320°, and 430°C which are most probably related to the reactions occurring in the heated system. The other small maxima result from the losses of hydration (111°C) or constitution water.

The original product was found to yield some new compounds during heating and one of these compounds is formed at 166°C, that is, in the temperature applied by the above authors[4-9] for drying. Therefore, the magnetic and spectroscopic studies were made both on the original products and on their derivatives formed after prolonged heating at temperatures corresponding to the three main maxima of the thermogravimetric curve. In order to obtain a clearer picture, the original product has been marked in tables and figures as «product A» and the subsequent products, formed at 166°, 320°, and 430°C, as B, C, and D, respectively.

Magnetic Properties. All the above compounds, the original product and the fractions formed after heating to the corresponding temperatures, were subjected to magnetic studies. The measurements were made by the Gouy method for three samples of each product. Since the magnetic susceptibilities obtained in this way are identical for three samples of the fraction C and fraction D, the table gives average values for these substances. In Table I the gram magnetic susceptibility is given as a function of temperature ranging from 90°–320°K: $\chi_g \cdot 10^6=f(T)$.

The products C and D were found to be antiferromagnetic since their magnetic susceptibilities have maxima at about 300°K (Neel point). Above that point, the susceptibility does not depend on the magnetic field intensity and obeys the Curie-Weiss law with a negative value of the constant. Below T_N the magnetic susceptibility decreases with decreasing temperature and shows a non-linear dependence on the magnetic field intensity. Therefore, the susceptibilities for both these products given in Table I are the approximate values obtained by the extrapolation of the function $\chi_g=f\left(\frac{1}{H}\right)$ to $\frac{1}{H}=0$, where H is the field intensity. Only for these extrapolated values the following relationship $\frac{1}{\chi_g}=f(T)$ has been obtained:

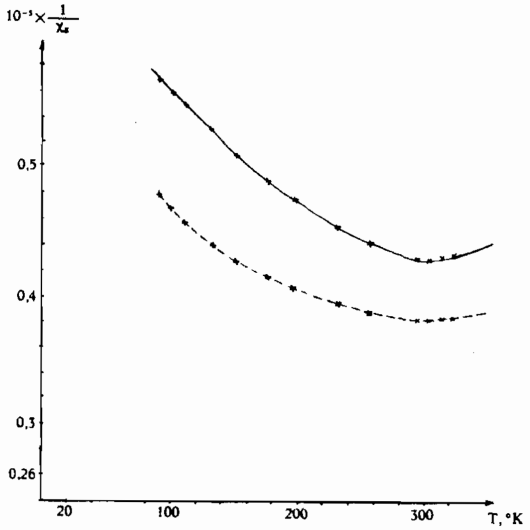

Figure 2. Relationship $1/\chi_g=f(T)$ for products C - - - - -, and D ———.

Table I.

Temp. [°K]	Product A 1	Product A 2	Product A 3	Product B 1	Product B 2	Product B 3	Product C	Product D
90	98.29	79.85	79.61	37.77	47.01	43.80	20.84	17.57
100	85.01	72.76	73.00	35.61	42.41	40.73	21.36	17.87
110	77.78	63.99	66.55	32.60	39.88	36.85	21.87	18.17
133	61.59	52.26	52,63	28.09	33.34	31.79	22.72	18.92
150	54.46	44.90	46.84	25.54	29.31	28.04	23.45	19.61
175	44.39	38.39	39.08	22.65	25.67	24.12	24.08	20.36
195	40.00	34.78	35.29	20.72	23.73	22.04	24.61	20.94
230	33.72	28.27	29.18	18.19	20.64	19.50	25.33	22.00
255	29.45	25.80	26.85	16.24	18.37	18.10	25.71	22.62
293	25.57	21.88	23.12	14.54	16.56	15.81	26.07	23.21
300	22.85	19.52	21.43	13.66	15.74	14.52	26.27	23.21
310	18.96	16.13	17.45	12.40	14.39	13.77	26.06	23.16
323	13.91	13.57	14.08	11.07	12.42	11.84	26.05	23.12

For the products A and B, with the assumed molecular weight of about 432 (which will be proven below) the following spin moments and Curie-Weiss constants have been obtained:

Table II.

	Product A			Product B		
	1	2	3	1	2	3
Θ°K	20	14	9	−30	−17	−21
μ_B [M.B.]	3.47	3.27	3.38	2.83	2.94	2.89

In order to obtain some more information, the electronic paramagnetic resonance studies were made. The width of the resonance line δ_H for the original complex is equal to 399 Oe, while the antiferromagnetic products have a much wider resonance line of 1217 Oe. This sudden broadening of the absorption lines at temperatures below the Neel point corresponds to the results of paramagnetic resonance studies on antiferromagnetics and was observed for the first time in powdered Cr_2O_3.[11]

Table III.

Compound	Infrared Spectra				
Cr_2O_3	413 s	444 s	475 vs	983 vs	
CrO_3	780 s	893 m	909 s	645 vs	
CrO_2	575 vs	895 m	940 w	968 vs	995 vs
$Cr(OH)_3$	510 vs	613 s			
K_2CrO_4	848 m(ν_1)	884 vs(ν_3)			

Infrared Spectra. The infrared spectra were made in an UR-10 spectrophotometer over the range 400-5000 cm^{-1}. Several simple chromium compounds have been investigated and the results of these studies enabled us to interpret the spectra by the band comparison method. On the basis of this method, the bands observed were assigned to the vibrations of the definite functional groups.

The infrared spectra of simple chromium compounds agree with those obtained by Wadier,[12] Strammreich,[13] Bassi[14] *et al.* Therefore, in the present work, only the results are given.

The products obtained, whose spectra are given in Table V, were subjected to detailed investigation.

The infrared spectra of products C and D are collected in Table VI.

Absorption and Reflection Spectra. As the compounds obtained in the reaction $Cr^{III}+Cr^{VI}$ are soluble neither in water nor in acidic and basic solutions, the spectra were recorded in the solid phase. Potassium bromide pellets were used at the ratio of substance: KBr = 1:200 (Figure 5). The reflection spectra were measured using MgO as a diluent at a ratio substance: MgO = 1:10 (Figure 3) and 1:2 (Figure 4). The results have been compared with the spectra of a number of simple Cr^{III} and Cr^{VI} compounds as Cr_2O_3, CrO_3, $Cr(OH)_3$, $K_2Cr_2O_7$, K_2CrO_4. The measurements were made in an Unicam SP 700 spectrophotometer over the range of 4000-55000 cm^{-1}.

In all cases, the bands characteristic of the Cr^{III} compounds were found. For these compounds the crystal field parameters and the Racah B coefficients were calculated. The spectra of simple chromium compounds were very helpful in these calculations.

The results are given in Table VII:

Table IV.

	ν_s(Cr—O—Cr)	ν_{as}(Cr—O—Cr)	$\nu_s(CrO_3)$	$\nu_s(CrO_3)$	$\nu_{as}(CrO_3)$
$K_2Cr_2O_7$	556 w	764 vs	885 s	902 ms	924 s, 946 vs 934 vs, 950 vs, 966 s
	566 w	796 ms	891 m	908 m	940 vs, 956 vs

Table V.

	ν_{as}(Cr—OH)	ν_s(Cr—O)	ν_s(Cr—OH—Cr)	ν(OH—Cr—OH) ν(O—Cr—O)	ν_{as}(Cr—O—Cr)	δ_s . OH ν_{as}(Cr—O)
Product A	505 vs	520 vs	—	—	820-840 vs	918 vs 952 s
Product B	510 m	525 m	574 s	772 m	863 m	920 s 960 s

Table VI.

Compound	Infrared Spectra									
Product C	409 m	447 m	485 s	—	648 s	780 m	893 m	909 m	968 m	—
Product D	412 m	445 w	475 s	585 vs	650 s	—	890 w	945 m	983 s	995 s

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[11] E. P. Trounsen, D. F. Bleil, R. K. Wangsness, and L. R. Maxwell, *Phys. Rev.*, *79*, 542 (1950).

[12] C. Wadier, C. Duval, and J. Lecomte, *Compt. Rend.*, *275-25*, 3766 (1963).

[13] H. Strammreich, D. Bassi, O. Sala, and H. Siebert, *Spectrochim. Acta*, *13*, 192 (1958).

[14] D. Bassi and O. Sala, *Spectrochim. Acta*, *12*, 403 (1958).

Table VII.

Compound	Band position (in cm^{-1})	Type of spectrum	Electron transition	Notes Δ, B (in cm^{-1})
Product A	5850	Absorption	Cr–Cr	
	15,240		${}^4A_2 \rightarrow {}^4T_2$	Δ = 15,240
	20,500 sh		${}^4A_2 \rightarrow {}^2T_2$	B = 585
	26,340		${}^1A_1 \rightarrow {}^1T_2\ (t_1 \rightarrow 2e)$	
	31,660 sh			
	38,630		${}^1A_1 \rightarrow {}^1T_2\ (3t_2 \rightarrow 2e)$	
	43,000			
	18,420 sh	Reflection	${}^4A_2 \rightarrow {}^4T_2$	Δ = 18,420
	26,280		${}^4A_2 \rightarrow {}^4T_1$ or ${}^1A_1 \rightarrow {}^1T_2\ (t_1 \rightarrow 2e)$	B = 645
	37,150		${}^1A_1 \rightarrow {}^1T_2\ (3t_2 \rightarrow 2e)$	
	43,980			
Product B	17,350	Reflection	${}^4A_2 \rightarrow {}^4T_2$	Δ = 17,350
	26,490		${}^4A_2 \rightarrow {}^4T_1$ or ${}^1A_1 \rightarrow {}^1T_2\ (t_1 \rightarrow 2e)$	B = 760
	34,930		${}^1A_1 \rightarrow {}^1T_2\ (3t_2 \rightarrow 2e)$	
	16,850	Absorption	${}^4A_2 \rightarrow {}^4T_2$	Δ = 16,850
	28,180		Cr–O–Cr or ${}^1A_1 \rightarrow {}^1T_2$	Ref. 15
	36,700		${}^1A_1 \rightarrow {}^1T_2\ (3t_2 \rightarrow 2e)$	
	41,760			
	48,250 sh			
Product C	17,270	Reflection	${}^4A_2 \rightarrow {}^4T_2$	$Cr^{3+} + CrO_3$
	21,150		${}^4A_2 \rightarrow {}^2T_2$	Δ = 17,270 B = 610
	28,520			
Product D	16,490	Reflection	${}^4A_2 \rightarrow {}^4T_2$	$Cr^{3+} + CrO_3$ Δ = 16,490
	21,630		${}^4A_2 \rightarrow {}^4T_1$	B = 620
	26,710			
	29,000		${}^3T_1 \rightarrow {}^3E, {}^3T_1, {}^3A_1, {}^3A_2$	Cr^{IV}
$Cr(OH)_3$	16,770	Reflection	${}^4A_2 \rightarrow {}^4T_2$	Δ = 16,770
	23,150		${}^4A_2 \rightarrow {}^2T_2$	B = 760
	25,000 sh			
	34,000-37,000 sh			
	16,840	Absorption	${}^4A_2 \rightarrow {}^4T_2$	Δ = 16,850
	22,930		${}^4A_2 \rightarrow {}^2T_2$	B = 655
	31,690 sh			
	37,000			
	49,000 sh			
Cr_2O_3	16,210	Reflection	${}^4A_2 \rightarrow {}^4T_2$	Δ = 16,210
	20,980		${}^4A_2 \rightarrow {}^2T_2$	B = 598, Ref. 16
	26,070		${}^4A_2 \rightarrow {}^4T_1$	
CrO_3	16,720 sh	Reflection		
	21,000 sh			
	26,430			
	34,870			
$K_2Cr_2O_7$	15,000 sh	Reflection		
	21,700 sh			
	27,000			
	36,150			
	9680 sh	Absorption		
	16,660 sh			
	21,500 sh			
	26,080			
	35,330			
	47,500			
K_2CrO_4	19,500 sh	Absorption		
	27,160		${}^1A_1 \rightarrow {}^1T_2\ (t_1 \rightarrow 2e)$	Ref. 17
	36,450		${}^1A_1 \rightarrow {}^1T_2\ (3t_2 \rightarrow 2e)$	Ref. 17
	46,420			
	51,700 sh			
	15,000-18,000 sh	Reflection		
	23,500 sh			
	26,940		${}^1A_1 \rightarrow {}^1T_2\ (t_1 \rightarrow 2e)$	Ref. 17
	35,310 sh			
	38,000		${}^1A_1 \rightarrow {}^1T_2\ (3t_2 \rightarrow 2e)$	Ref. 17

Results and Discussion

On the basis of spectroscopic and magnetic studies, it is possible to establish some general structural features of the products obtained. Frauss and Gnatz,[1] as wel las King and Neptune,[2] suggested, on the basis of their optical and potentiometric studies on chromium solutions, that the solutions contain soluble complexes of formula $[Cr(OH)_2]HCrO_4$. Moreover, these authors suggest that the brown insoluble product formed in these solutions has the formula $[Cr(OH_2]_2CrO_4$. Our

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(15) C. E. Schöffer, *J. Inorg. Nuclear Chem.*, *8*, 149 (1958).
(16) R. A. Ford and O. F. Hill, *Spectrochim. Acta*, *16*, 1318 (1960).
(17) A. Viste and H. Gray, *Inorg. Chem.*, 3, 1113 (1964).

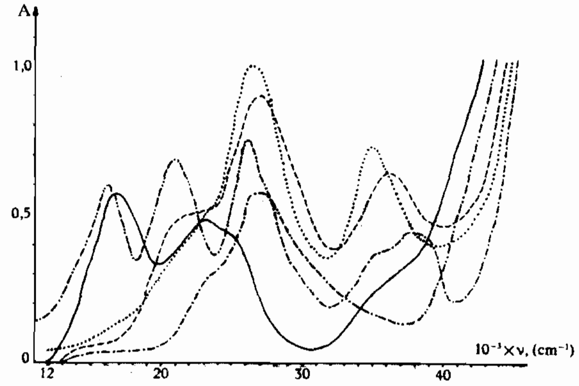


Figure 3. Reflection spectra: $Cr(OH)_3$ ———; Cr_2O_3 - - - - - - - -; CrO_3 . . . .; $K_2Cr_2O_7$ - - - - - - -; K_2CrO_4 - - - - - - - - -

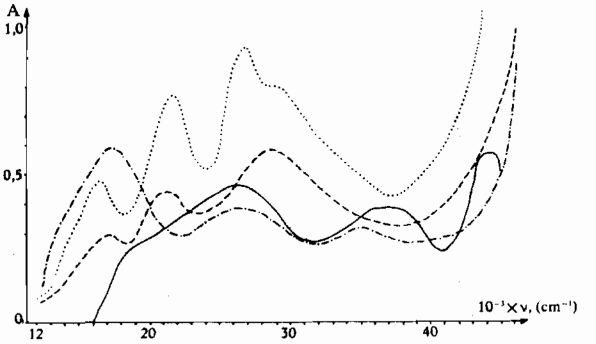


Figure 4. Reflection spectra: product A ———; product B - - - - - - - - -; product C - - - - - - - - -; product D . . . .

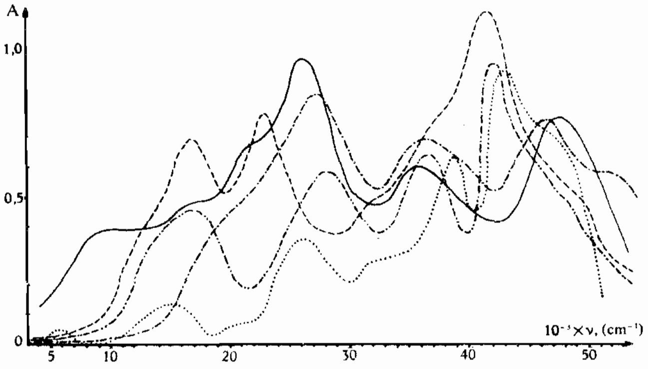
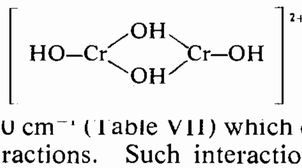


Figure 5. Absorption spectra in solid: product A . . . .; product B - - - - - - - -; $Cr(OH)_3$ - - - - - - - -; $K_2Cr_2O_7$ ———; K_2CrO_4 - - - - - - -

studies provided some evidence to support this concept, since there are many data suggesting that the brown product precipitated directly from solution is a mixture of two compounds whose structures are as follows:



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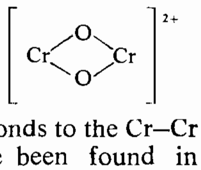
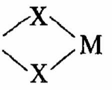
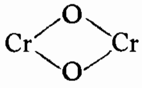
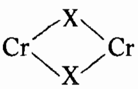


5850 $\mathrm{cm^{-1}}$ (Table VII) which corresponds to the Cr–Cr interactions. Such interactions have been found in compounds having the  structure.[18] There is also other evidence the μμ'diolic bond has no active vibrations over the range 700-900 $\mathrm{cm^{-1}}$ [19] while we have found a broad, diffuse band at 820-840 $\mathrm{cm^{-1}}$ (Table V). This is due to the Cr–O–Cr bond vibrations occurring in the functional group  which should be active only in the region 700-860 $\mathrm{cm^{-1}}$.[20]

The absorption and reflection spectra of the product A (Figures 4 and 5) show a number of bands resulting from the electronic transitions in Cr^{III} and the bands characteristic of CrO_4^{2-} correspond to the values given by Jørgensen.[21]

Magnetic measurements of the original product give the average moment 3.37 BM (Table II) which agrees with the theoretical calculation made by Earnshaw and Lewis[22] taking into account the Cr–Cr interactions for $\mathrm{chromium^{III}}$

A certain change of properties was observed on heating the original product up to 166°C. No band resulting from the Cr–Cr interaction appears in the near infrared which is an evidence that the  structure disappears. Some new complexes are probably being formed with the linear structure of a Cr–O–Cr or Cr–OH–Cr type. The band at 574 $\mathrm{cm^{-1}}$ (Table V) was assigned to the symmetric vibrations of the Cr–OH–Cr system, whereas the band at 863 $\mathrm{cm^{-1}}$ probably results from the asymmetric vibrations of the bridge oxybond Cr–O–Cr. The simultaneous appearance of both these bands shows that, here again, a mixture of complexes is observed with the structures: –Cr–O–Cr– and –Cr–OH–Cr–. The band at 772 $\mathrm{cm^{-1}}$ is rather uncertain since it may be formed from two effects. First, it may result from vibrations of the linear systems O–Cr–O and HO–Cr–OH which take place in the chains –X–Cr–X–Cr–, that is, during the thermal polymerisation, a mixture of bi- and polynuclear products with the oxygen and olic bonds may be formed. Second, the formation of $Cr^{III}–O–Cr^{IV}$–like bonds, whose asymmetric vibrations should absorb in the range 760-840 $\mathrm{cm^{-1}}$ is probable. It is hard to decide which one of these structures should be assigned to the product. The simultaneous occurrence of both these structures is probable.

It is also difficult to establish univocally the origin of the band at 28180 $\mathrm{cm^{-1}}$ (Table VII) in the absorption spectra of the product B as the absorption band resulting from electron transitions inside the bridge $Cr–O–Cr$[15] may be found near this frequency and also the transition $^1A_1 \rightarrow {}^1T_2$ $(3t_2 \rightarrow 2e)$ appearing in the CrO_4^{2-} anion.

Similar evidence is provided by the magnetic measurements. An average moment 2.89 BM is considerably different from that obtained for the product A

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(18) W. Wojciechowski, B. Jeżowska-Trzebiatowska, and M. Rudolf, *Chem. Zvesti*, *19*, 229 (1965).

(19) D. J. Hewkin and W. P. Griffith, *J. Chem. Soc.*, 472 (1966); ... complexes'', Pergamon Press, Oxford-London, New York, Paris, p. 110 (1962).

(22) A. Earnshaw and J. Lewis, *J. Chem. Soc.*, 396 (1961).

(Table II). This decrease in paramagnetism or partial pairing of the spins results from the oxygen bond Cr–O–Cr formed in the system.[12]

At 320°C further transformation of the system occurs. The product C has different properties from the previous compounds. It is dark green while the compounds A and B were brown. The infrared bands become broad and diffuse and have a very complex structure with numerous shoulders whose positions clearly show that it is a mixture of Cr_2O_3 and CrO_3. The infrared spectrum (Table VI) corresponds exactly to that expected for the system: $Cr_2O_3 + CrO_3$. Similar conclusions may be drawn from the reflection spectra (Figures 3 and 4) and magnetic studies (Table I, Figure 2). The antiferromagnetic properties of the product C and the broadening of the electronic paramagnetic resonance absorption line result from chromium(III) oxide.

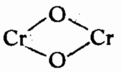
The final product obtained on heating the original product up to 430°C differs from the product C only in its spectroscopic properties.

The infrared bands maintain their structure but the spectrum becomes similar to that expected for the mixture $Cr_2O_3 + CrO_2$. It is most probable that the disproportionation $Cr^{III} + Cr^{VI} \rightarrow Cr^{VI}$ occurs here to a very slight extent and the remaining quantity (about 92% ot Cr^{VI}) is being reduced by exposure to air to Cr^{III}. The structure of the product D may be of the chain type —O–Cr–O–Cr–O— as suggested by Wadier *et al.*[12]

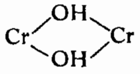
The bands at 26710 and 29000 cm^{-1} occurring in the reflection spectrum of the product D result most probably from the electron transitions from term $^3T_1$ to one of the CrO_2 terms. The assignment, however, is difficult.

Conclusion

It was found that some doubtful brown products formed in solutions containing Cr^{III} and Cr^{VI} are the mixtures of complexes of the formulae $[Cr(OH)_2(H_2O)_4]_2CrO_4$ and $[CrO(H_2O)_4]_2CrO_4$, which consist of the groups:



and



On drying at about 130°C, these compounds are converted into the linear complexes Cr–O–Cr, Cr–OH–Cr, –Cr–X–Cr–X— (where X = O, OH) or Cr^{III}–O–Cr^{VI}. Above 200° the compounds decompose with a simultaneous partial reduction of chromium(VI) to chromium(III) until the mixture of oxides $Cr_2O_3 + CrO_2$ is formed. At about 430°C partial disproportionation $Cr^{III} + Cr^{VI} \rightarrow Cr^{IV}$ and simultaneous reduction $Cr^{VI} \rightarrow Cr^{III}$ occur, with exposure to air.