complex $[enH_2][V(hedta\text{-}H)]_2 \cdot 2H_2O$,[44] and the Fe^{III}_2–hedta complex $[enH_2][Fe_2O(hedta)_2]$.[45] $((NH_3)_5RuOV(hedta))^+$ has also been identified in solution by EPR.[13] That $Ti^{III}Ti^{IV}(hedta)_2$ and $Ti^{IV}V^{III}(hedta)_2$ complexes are blue and orange is not surprising in light of the blue and green colors imparted to corundum by Ti^{IV}–O–Fe^{III} and Fe^{III}–O–Fe^{II} impurities.[46]

Equilibrium studies of eq 11 are hindered by the competitive dimerization of $V(hedta)(OH)^-$ in the pH range 4.9–5.2 (eq 12) and by the precipitation problems of $TiO(hedta)^-$ solutions

$$2V(hedta)(OH)^- \rightleftharpoons (V(hedta\text{-}H))_2{}^{2-} \qquad (12)$$

in this range. Studies at pH ~5 were carried out as a perturbation of equilibrium 11 by the reaction in eq 12. The $Ti^{IV}V^{III}$ binuclear ion is fully formed when [Ti(IV)]:[V(III)] is 1:50. Under these conditions $\epsilon_{453} = (3.8 \pm 0.1) \times 10^2$ M^{-1} cm^{-1}. By varying the ratio of reactants, we found an equilibrium constant for eq 11 to be 5.0×10^2 M^{-1} ($\mu = 0.50$ (NaCl), $T = 25.0$ °C). The forward rate of formation (eq 11) was easily followed at 453 nm in the stopped-flow studies after 50 s. The formation rate followed second-order kinetics under equal initial concentrations of Ti(III) and V(IV), or Ti(IV) and V(III), after 50 s. The measured rate constant is 23.1 M^{-1} s^{-1} ($\mu = 0.50$ (NaCl), $T = 25.0$ °C). Combination of this value with the measured association constant of 500 M^{-1} yields a rate constant for dissociation of 4.6×10^{-2} s^{-1}. This result is within a factor of 10 of the breakup of the V^{III}_2 and Fe^{III}_2 species; it is therefore quite reasonable for either the dihydroxy- or oxo-bridged structures. The overall stability constant for $Ti^{IV}V^{III}$ of 5.0×10^2 M^{-1} is comparable to that for the Fe^{III}_2 complex (2.4×10^2)[35] and 10-fold smaller than the V^{III}_2 value (5.5×10^3 M^{-1}).[25] The rate of formation (23 M^{-1} s^{-1}) is 15 times slower than the forward dimerization reaction in eq 12, suggesting that more reorganization is required at the $TiO(hedta)^-$ center than for $V(hedta)(OH)^-$.

The fact that the $Ti^{IV}V^{III}$ species is not formed in the initial steps of the cross reaction of $Ti(hedta)(H_2O)$ and $VO(hedta)^-$ is definitive in showing that the dominant electron-transfer process between these complexes is outer sphere in nature. Such a process should be first order in each of the Ti(III) and V(IV) species unless the redox process is limited by a slow step as described in eq 5.

The orange color of the Ti^{IV}–V^{III} binuclear species is similar to the orange color of the peroxo complex of $Ti(edta)(O_2)^{2-}$. Since $TiO(hedta)^-$ is colorless in the visible region, the presence of an electron-rich chromophore coordinated to Ti(IV) is required for the appearance of the charge-transfer band. This is similar to the ligand to metal CT in the peroxo complex. Coordination of V(III) to an oxo ligand makes the Ti–O–V chromophore appropriately electron rich for a similar MLCT transition.[46]

Acknowledgment. Acknowledgment is made to the donors of the Petroleum Research Fund, administered by the American Chemical Society, for support of this research.

Registry No. $Ti(hedta)(H_2O)$, 75431-40-2; $VO(hedta)^-$, 62560-22-9; $(hedta)TiOV(hedta)^-$, 75716-19-7; $TiO(hedta)^-$, 75431-41-3; $V(hedta)(H_2O)$, 75431-42-4.

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(47) If only $[TiO(hedta)^-]_{added}$ is used to evaluate rate constants instead of $[TiO(hedta)^-]_{av}$ in eq 8, the following constants are obtained (375 nm): $a = 0.23 \pm 0.08$ s^{-1}, $b = (3.17 \pm 0.37) \times 10^2$ M^{-1} s^{-1}. Hence the *b* path values are unchanged within experimental error. A reviewer has asked why a reiterative type of fit, utilizing the instantaneous amount of $[TiO(hedta)^-]$, was not attempted for eq 8. This would require a knowledge of rate constants for all parallel redox pathways that generate $TiO(hedta)^-$ to a greater accuracy than seem valid from this study. In addition, there may be other species that exist at equilibrium in this pH range with the dominant form $TiO(hedta)^-$ such as $TiO(hedta)(H_2O)^-$ and $TiO(Hhedta)(H_2O)$. Each of these may differ kinetically or may be produced at different rates via the redox reactions producing Ti(IV). For example, the reactions of H_2O_2 with $TiO(edta)^{2-}$, $TiO(edta)^{2-}$, and $TiO(Hedta)(H_2O)^-$ have widely different reactivities toward H_2O_2 (F. Kristine and R. E. Shepherd, submitted for publication in *Inorg. Chem.*). Since the distribution of fully and partially chelated species for $TiO(hedta)^-$ is not certain, a reiterative approach would not produce additional meaningful results, relatable to a single molecular species.

(48) The *b* path proceeds at least a factor of 3 times faster than any *a* path. Using $[TiO(hedta)^-]_{av}$ the magnitude of *a* approaches zero within experimental error. However if $[TiO(hedta)^-]_{added}$ is used in evaluating eq 8, the value of *a* obtained at 375 nm (0.23 ± 0.08 s^{-1}) agrees quite well with the value obtained from relaxation methods for the monomerization of $Ti^{III}_2(hedta)_2$: 0.23 ± 0.01 s^{-1}. A convenient interpretation of all of these results would be shown with absorbance changes first order in $Ti^{III}_2(hedta)_2$:

$$Ti^{III}_2 + Ti^{IV} \xrightarrow{b} Ti^{III}Ti^{IV} + Ti^{III}$$

$$Ti^{III}_2 \overset{a}{\rightleftharpoons} 2Ti^{III}$$

$$Ti^{III} + Ti^{IV} \xrightarrow{\text{fast}} Ti^{III}Ti^{IV}$$

Contribution from the Refractories and Building Materials Laboratory,
National Research Centre, Dokki, Cairo, Egypt

Valency of Chromium in the Equilibrium Ternary Phase Belonging to the Noncondensed System $CaO\text{–}Cr_2O_3\text{–}O_2$

E. A. EL-RAFEI

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In the title system the three equilibrium phases—the ternary compound, calcium chromate, and monocalcium chromite—were synthesized. The solid-state IR, diffuse-reflectance, and ESR spectra of the ternary phase were compared with those of the two other phases to reveal the valency of chromium in this phase *in solid state*. The different spectral results were communicated and interpreted. The absence of Cr^{III} was confirmed and the presence of $Cr^VO_4{}^{3-}$ tetraoxoanion was strongly suggested in the composition of the solid ternary phase. Hence, the ternary phase has *in the solid state* the tricalcium orthochromate formula $Ca_3(Cr^VO_4)_2$ rather than the chromate chromite formula $Ca_9(Cr^{VI}{}_4Cr^{III}{}_2)O_{24}$, which describes the composition of the ternary phase in acid solutions.

Introduction

The study of solid-state chemistry of the equilibrium phases based on the noncondensed $CaO\text{–}Cr_2O_3\text{–}O_2$ system has definite importance in the chemistry of transition-metal ions involving oxo ligands as well as the manufacture and service of basic refractories.

Three equilibrium phases—monocalcium chromite ($CaCr^{III}{}_2O_4$), calcium chromate ($CaCr^{VI}O_4$), and a ternary

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compound—are known[1] to exist in the ternary system $CaO–Cr^{VI}O_3–Cr^{III}{}_2O_3$ at molar $CaO:Cr_2O_3$ ratios 1:1, 2:1, and 3:1, respectively.

The first binary phase, monocalcium chromite, is a high-melting (mp 2170 °C[1]) phase. It exists in high- (α) and low- (β) temperature modifications.[1] The β[2] and α[3] modifications were used for manufacturing different high-quality refractory materials for various industrial purposes. The α form[4] as well as the β modification[5] has orthorhombic symmetry.

The second binary phase, calcium chromate ($CaCr^{VI}O_4$), dissociates[1] at 1022 °C into the high-melting monocalcium chromite and a ternary phase having a calcium:chromium ratio 3:2.

Among the numerous ternary phases, having different $CaO:CrO_3:Cr_2O_3$ ratios, i.e., having chromium in a valency other than 3+ or 6+, reported[1] to exist in the noncondensed $CaO–Cr_2O_3–O_2$ system, it has been shown[6] that the equilibrium ternary phase (hereafter referred to as the ternary phase) is that one having a calcium:chromium ratio 3:2. This phase was produced[7] on heating in air at 1200 °C a mixture having a molar $CaO:Cr_2O_3$ ratio 3:1 or by heating in air at 800 °C a mixture of calcium chromate and CaO at molar ratio 2:1. The ternary phase is also developed in refractories based on the multicomponent system $CaO–MgO–SiO_2–Al_2O_3–Fe_2O_3–Cr_2O_3–O_2$ at a molar $CaO:SiO_2$ ratio ≥ 2.[6,8]

The ternary phase is a low-melting (1228 °C[7]) compound; however, it has many advantageous refractory characteristics: it reversibly transforms at its melting point into the high-melting monocalcium chromite,[9] hence improving the refractoriness under a load of basic refractories;[10] it improves also the sintering of refractory lime-clinker;[11] and its hydraulic properties[1] make possible the production of high-quality basic refractory concretes[12] and cements.[13]

Since the ternary phase was first reported[1] in 1937, it has been assigned *either* of these two formulas.

(a) Chromate Chromite Formula. This contains both Cr^{VI} and Cr^{III} in the ratio 2:1 for a total of six chromium atoms. This formula has resulted from the chemical analysis of acid solutions of this ternary phase without investigation in the solid state.[1,7,9,14] The chromate chromite formula has been given any of these representations: (i) $9CaO\cdot4CrO_3\cdot Cr_2O_3$;[1,6,7,9–14] (ii) $Ca_9(Cr^{VI}{}_4Cr^{III}{}_2)O_{24}$;[15] (iii) $Ca_9Cr_6O_{24}$.[16]

(b) Oxychromite Formula. This contains Cr^V. The following representations have been given to this formula: (i) $3CaO\cdot Cr_2O_5$,[1] which was given without analytical evidence; (ii) tricalcium orthochromate ($Ca_3(Cr^VO_4)_2$), which was not substantiated by direct measurements but has been postulated[17] on the basis of the structural analogies with β-$Ca_3(PO_4)_2$; (iii) $Ca_3Cr_2O_8$,[18] which has been reported without proving the existence of Cr^V.

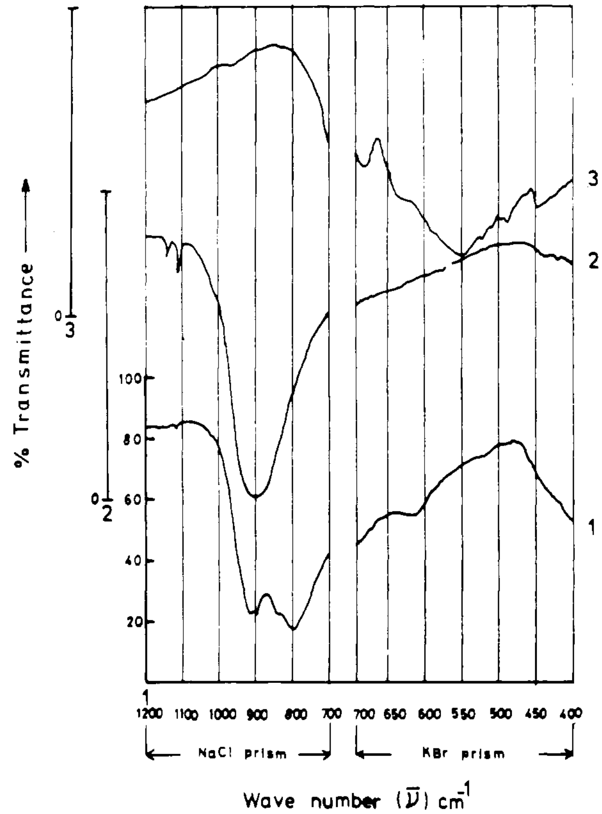

Figure 1. Solid-state infrared absorption spectra of the three equilibrium phases: 1, ternary phase; 2, calcium chromate; 3, β-monocalcium chromite.

However, the synthesis of different quinquevalent chromium compounds has been reported in the last two decades, e.g., alkali,[19] alkali earth,[20,21] chromate(V) (containing the tetraoxo species $Cr^VO_4{}^{3-}$), the tetraoxoanion $Cr^VO_4{}^{3-}$ in aqueous KOH solution,[22] the compounds of this tetraoxo species with apatite,[23] hydroxyapatite,[14,20,23] spodiosite,[23,24] etc. The crystal structure of these compounds has been studied.[19–21,25,26]

Nevertheless, until now many authors had described the composition of the ternary phase by the chromate chromite formula, and there have been hardly any systematic investigations on the constitution of the equilibrium phases in the title system in the solid state.

The purpose of the present work is to study in the solid state the IR, the diffuse-reflectance, and the ESR spectra of the synthesized three equilibrium phases to gain knowledge of the valence state of chromium in the ternary phase, i.e., whether it has the tricalcium orthochromate formula (Cr^V) or the chromate chromite formula (both Cr^{VI} and Cr^{III}).

Experimental Section

Synthesis of the Equilibrium Phases. Calcium chromate, β-monocalcium chromite, and the ternary phase were prepared from

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Table I. Solid-State Infrared Absorption Spectra of the Three Equilibrium Phases in Comparison with Relevant Spectral Results[a]

		abs freq, cm^{-1}					
ref	phase	$\nu_1(A_1)$	$\nu_3(F_2)$			other strong bands	site symm
this work	ternary phase	615 w	920 s	895 s	835 sh	795 s	$\leqslant C_{2v}$
32	$Ca_3(Cr^VO_4)_2$	770 sh	920 w	895 s	850 s		
33	$Ca_3(Cr^VO_4)_2$	863 s	817 s	766 s	713 s		
24	$Ca_2Cr^VO_4Cl$	712	865	810	760		C_2
24	$Ca_5(Cr^VO_4)_3Cl$	770	850	822			
34	$Ba_3(Cr^VO_4)_2$	824 w	868 m	855 s	844 w	762	
this work	calcium chromate		905 vs				T_d
35	Ca^{2+}–$Cr^{VI}O_4^{2-}$ (doped KBr)		903 vs				T_d
32	$CaCr^{VI}O_4$		880 s				D_{2d}
29	$CaCr^{VI}O_4$		890 vs				

		abs freq, cm^{-1}							
		$\nu_4(F_{1u})$ + $\nu_5(F_{2g})$	$\nu_3(F_{1u})$	$\nu_5(F_{2g})$ + $\nu_6(F_{2u})$	Cr–O str vib				
this work	β-monocalcium chromite	680 s	640 sh	555 s, b	525 w	510 w	500 w	475 m	445 m

[a] w = weak; m = medium; s = strong; vs = very strong; b = broad; sh = shoulder. $\nu_1(A_1)$ and $\nu_3(F_2)$ = the symmetric and the asymmetric Cr–O stretching modes, respectively, in the tetraoxoanions $Cr^VO_4^{3-}$ and $Cr^{VI}O_4^{2-}$. $\nu_3(F_{1u})$ = IR-active Cr–O stretch; $\nu_4(F_{1u})$ = IR-active O–Cr–O deformation mode; $\nu_5(F_{2g})$ = Raman-active O–Cr–O deformation frequency; $\nu_6(F_{2u})$ = inactive O–Cr–O bend in the octahedral Cr^{III} ion possessing O_h symmetry.[31]

analytically pure BDH grade $CaCO_3$ and Cr_2O_3 by heating the appropriate molar ratios *in air* at the required firing temperature. The procedure of synthesis and the X-ray diffraction patterns of the three phases obtained were published in our previous work.[9]

IR Spectra. The spectra of the different phases in KBr press were recorded in the region 400–1200 cm^{-1} at room temperature on a UR 10 Karl Zeiss fully automatic IR spectrophotometer at double-beam position and optimum slit width.

Optical Spectra. The spectra of the solid samples were measured by means of diffuse reflectance in the spectral range 10×10^3–32×10^3 cm^{-1} by using a Unicam SP 500 spectrophotometer. A constant slit width was used throughout to avoid large errors, since on variation of slit width the light falls on a curved surface.[22] The samples were compared to a standard of pure MgO. The corresponding curves were obtained by plotting the wavenumber $\bar{\nu}$ vs. the remission function calculated according to the Kubelka–Munk equation: $\log (K/S) = (1 - R)^2/2R$, where K and S are the absorption and scattering coefficients, respectively, and R is the reflection from the sample.[27] The absorption spectra of solutions were recorded on the same spectrophotometer, and the corresponding curves were produced by plotting $\bar{\nu}$ vs. the optical density.

ESR Spectra. A Varian V-4502 EPR spectrometer equipped with a mark I Fieldial and a V-4537 TE_{102} cavity, operating at a frequency of 9.25 GHz (9.25×10^9 Hz), was used for all ESR measurements. Finely powdered samples of each of the equilibrium phases were placed in glass tubes (2-mm diameter and 100-mm length) which were then placed in the microwave cavity. All measurements were conducted at room temperature. Instrumental limitations prevented carrying out experiments at 4–77 K.

Results and Discussion

(A) Absorption Spectroscopy. (a) Produced Spectra. The spectrum of the ternary phase is completely different from the spectra of calcium chromate and β-monocalcium chromite (Figure 1) not only in number and position of bands but also in the magnitude of absorption. The spectrum of the ternary compound contained neither the peak at 905 cm^{-1}, characteristic of the tetraoxo species $Cr^{VI}O_4^{2-}$ [28,29] in the spectrum of calcium chromate, nor the absorption maxima in the spectral range 440–680 cm^{-1}, specific of the octahedrally coordinated Cr^{III} ion[30,31] in the spectrum of β-monocalcium chromite.

Table I records the position of different observed bands with an estimate of their relative intensities and their assignments. Also included are the site symmetries of the different anions comprising the investigated phases and the relevant published spectral data for comparison.

The absence of absorption lines in the spectral range 550–580 cm^{-1},[29,31] specific for Cr_2O_3, is good evidence concerning the completion of synthesis reactions of the investigated phases.

The experimental results in Table I are, in general, in good agreement with corresponding spectral data. However, the slight difference in some band positions as well as the relative estimated intensities compared with the tabulated literature data can be, most probably, ascribed to instrumental[24,29–35] and preparative[32] differences.

(b) Spectral Assignment. The spectra obtained for the three investigated phases (Figure 1 and Table I) were interpreted on the basis of relevant IR spectral data[24,28–35] and character tables as well as molecular and site symmetry analyses.[24,28,29,34]

(1) Ternary Phase. The spectrum of this phase is comparable with the IR patterns for the tetraoxoanion $Cr^VO_4^{3-}$ either in tricalcium,[32,33] tristronium, and tribarium orthochromates[32,34] or in chlorospodiosite.[24]

The weak band at 615 cm^{-1} in the spectrum of this phase was assigned to $\nu_1(A_1)$, and the strong bands at 920 and 895 cm^{-1} as well as the shoulder at 835 cm^{-1} were ascribed to the three components of $\nu_3(F_2)$. This assignment was based on (i) the resolution of the latent $\nu_1(A_1)$ mode, which is forbidden[24] for undistorted T_d symmetry, and (ii) the lift of F_2 degeneracy of ν_3 mode.[29]

The assignment of $\nu_3 > \nu_1$ is in favor of many works concerning the distorted tetrahedral oxoanion $Cr^{VI}O_4^{2-}$ [28,29,35] as well as the tetraoxo species $Cr^VO_4^{3-}$.[24,28,32]

The strong band at 795 cm^{-1} in the spectrum of the ternary phase, which seems to correspond to the unexplained band at

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Table II. Visible and Ultraviolet Absorption Maxima (10^3 cm^{-1}) of the Three Equilibrium Phases Compared with Related Literature Results

$Cr^VO_4^{3-}$			$Cr^{VI}O_4^{2-}$		Cr^{III}		
ref	first band	second band	ref	first band	ref	first band	second band
this work	16.00	27.78	this work	27.03	this work[j]	16.12	21.74
22[a]	16.00	28.17	22[d]	26.92	this work[k]	17.40	24.40
24[b]	17.00	27.94	41[e]	26.66			
40[c]	17.00	28.00	38[f]	27.00	45[l]	17.40	24.30
			42[g]	26.80	46[m]	17.48	24.50
			43[h]	26.60	22[n]	16.80	23.26
			44[i]	26.60	47[o]	16.20	22.70
					38[p]	16.30	21.50
					38[q]	17.00	23.30

[a] $Cr^VO_4^{3-}$ anion in aqueous KOH solution. [b] Chlorospodiosite doped with the tetraoxoanion $Cr^VO_4^{3-}$. [c] The same material studied at 80 K. [d] The tetraoxo species $Cr^{VI}O_4^{2-}$ in dilute alkaline solution. [e] Solid $BaCr^{VI}O_4$, $Na_2Cr^{VI}O_4$, and $K_2Cr^{VI}O_4$. [f] $MgCr^{VI}O_4$ crystals. [g] Neutral and alkaline aqueous solutions of $K_2Cr^{VI}O_4$. [h] $K_2Cr^{VI}O_4$ crystals in K_2SO_4. [i] $Cr^{VI}O_4^{2-}$ anion doped K_2SO_4 and Na_2SO_4 crystals. [j] β-$CaCr^{III}{}_2O_4$ crystals. [k] Solution of the ternary phase in 4 N $HClO_4$. [l] Solution of $KCr(SO_4)_2 \cdot 12H_2O$. [m] Hexahydrate ion $[Cr(H_2O)]^{3+}$. [n] Chrome alum in 8 M solution of KOH. [o] MgO crystals doped with Cr^{III} ions. [p] $LaCr^{III}O_3$ crystals. [q] $MgCr^{III}{}_2O_4$ crystals.

762 cm^{-1} in the spectrum of $Ba_3(Cr^VO_4)_2$[34] (Table I), may be attributed[36] to the activity of a combination between ν_1 and the low-frequency lattice mode. This band may be an indication of the high distortion[37] of $Cr^VO_4^{3-}$ tetrahedra in the ternary phase. On the other hand, the proposed interpretation[38] for the two bands in addition to the three components of ν_3 frequency in the spectrum of $MgCr^{VI}O_4$ (having the tetraoxo species $Cr^{VI}O_4^{2-}$ modified to C_{2v} symmetry), due to formation of a chain of $Cr^{VI}O_4^{2-}$ tetrahedra, seems unlikely in our case since chromate(V) is known[25,26] to have discrete $Cr^VO_4^{3-}$ tetrahedra. This fact also eliminates the possibility of ascribing the band at 795 cm^{-1} to the stretch of the Cr–O–Cr bridging oxygen, which is known[37] to be diagnostic of dichromate and polychromate(VI) chains and occurs near 770 cm^{-1}.

The small separation (25 cm^{-1}) between the maxima at 920 and 895 cm^{-1} suggests[36] that these bands could be due to a further splitting of one of the components of the ν_3 mode by interionic coupling.

On the basis of the character tables and molecular and site symmetry analyses,[24,28,34] the IR absorption spectrum of the ternary phase reveals that the molecular symmetry of the tetraoxo species $Cr^VO_4^{3-}$ in the lattice of this phase is $\leq C_{2v}$, i.e., either C_{2v} or C_2 (monoclinic system). The exact site symmetry of the tetraoxoanion could not be confirmed because the employed IR spectrophotometer permits recording only from 400 cm^{-1}, without ascertaining the symmetric $\nu_2(E)$ and the asymmetric $\nu_4(F_2)$ bends. The latter are known[28,32,33] to absorb below 400 cm^{-1}.

The modification of $Cr^VO_4^{3-}$ tetrahedron from ideal T_d symmetry to a lower one in the spectrum of the ternary phase is in good agreement with the previous work citing C_2 site symmetry of the tetraoxo species $Cr^VO_4^{3-}$ in chlorospodiosite.[24]

(2) Calcium Chromate. The strong band at 905 cm^{-1}, assigned to the unsplit $\nu_3(F_2)$, is in good agreement with the previous IR absorption spectral data of undistorted $Cr^{VI}O_4^{2-}$.[28,29,35] The absence of any other absorption frequencies in the spectrum of this phase (Figure 1 and Table I) conforms with T_d site symmetry.[28,29]

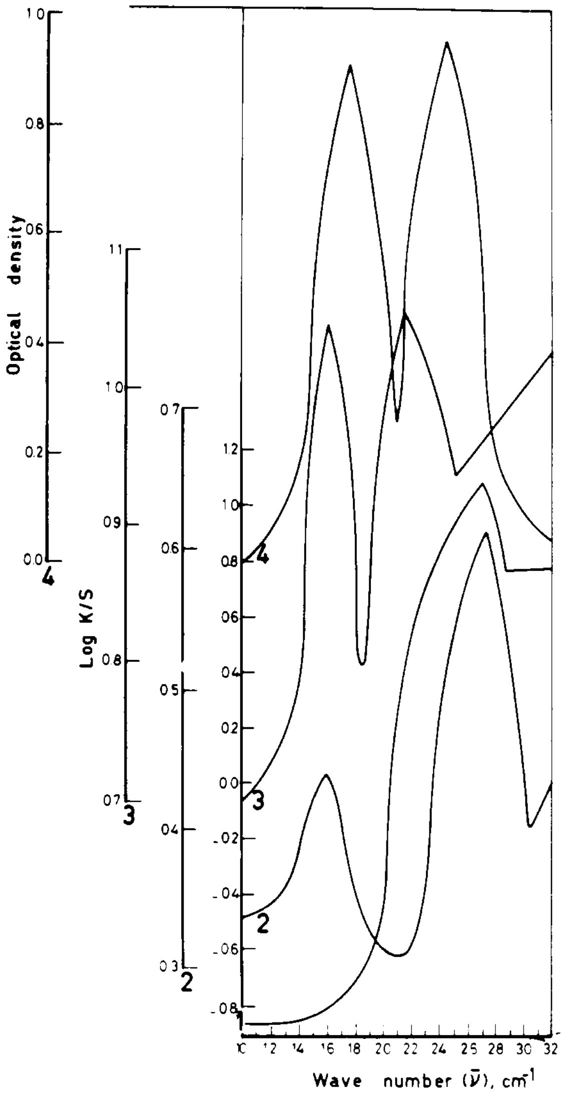

Figure 2. Diffuse-reflectance spectra of calcium chromate (1), ternary phase (2), and β-monocalcium chromite (3) and the absorption spectrum of a 3×10^{-2} M solution of the ternary phase in 4 N $HClO_4$ (4).

(3) β-Monocalcium Chromite. The IR absorpiton pattern of this phase is comparable with the relevant spectra of $MgCr^{III}{}_2O_4$[38] and Cr_2O_3.[29,31] The bands in the spectral region 555–680 cm^{-1} were assigned analogously to the IR spectral results of the octahedrally coordinated Cr^{III} ion possessing O_h symmetry.[31] Meanwhile, the absorption frequencies in the range 445–525 cm^{-1} were ascribed[30] to Cr–O stretching vibrations (see Table I).

Moreover, the IR absorption spectral results of the three investigated phases support the previously reported observation,[39] pointing out a regular decrease in the Cr–O stretching frequency as the oxidation state of chromium decreases.

(B) Optical Spectroscopy. (a) Diffuse-Reflectance Spectra. Hardly any studies have been carried out, until now, on the diffuse-reflectance spectroscopy of $Ca_3(Cr^VO_4)_2$, $CaCr^{VI}O_4$, and β-$CaCr^{III}{}_2O_4$. Table II records the different absorption maxima observed in the diffuse-reflectance spectra of the three synthesized phases as well as the peaks in the absorption spectrum of the Cr^{III} ion in $HClO_4$ solution. Also are included the relevant spectral data reported on the tetraoxo species

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$Cr^{V}O_4^{3-}$ [22,24,40] and $Cr^{VI}O_4^{2-}$ [22,38,41–44] as well as the Cr^{III} ion.[22,38,45–47] Note the good agreement between the experimental values and the corresponding reported spectral results.

In Figure 2 curves 1–3 show that the bands in the diffuse spectrum of the ternary phase are quite different from the peaks in the reflectance spectra of $CaCr^{VI}O_4$ and β-$CaCr^{III}{}_2O_4$ not only in the band position but also particularly in the magnitude of absorption. This was also the case[22] for the absorption spectrum of $Cr^{V}O_4^{3-}$ anion in aqueous KOH solution in comparison with the spectra of the $Cr^{VI}O_4^{2-}$ anion and Cr^{III} ion in aqueous alkaline solution.

(b) Absorption Spectra. The ternary phase was completely soluble in 4 N $HClO_4$ solution, which is known[20] as a preferential solvent of chromate(V). Curve 4 of Figure 2 depicts the absorption spectrum of the ternary phase in $HClO_4$ solution. It is quite clear that this spectrum is absolutely unlike the reflectance spectrum of the ternary phase (curve 2 of Figure 2). This was explained by the disproportionation of Cr^{V} in the ternary phase on its dissolution in $HClO_4$, which proceeds according to the equation[22] $3Cr^{V} \rightarrow 2Cr^{VI} + Cr^{III}$. Clear evidence of this was obtained by plotting the absorption spectrum of a synthetic mixture of Cr^{VI} ($CaCr^{VI}O_4$) and Cr^{III} ($Cr^{III}Cl_3$) in 0.1 N HCl solution in the molar ratio 2:1. This spectrum was quantitatively identical with the absorption spectrum of the ternary phase in $HClO_4$ solution (curve 4 of Figure 2). This result is in harmony with the reported[22] spectroscopic data for the $Cr^{V}O_4^{3-}$ anion in 8 M KOH solution and for an alkaline solution of $Cr^{VI}O_4^{2-}$ and Cr^{III} in molar ratio 2:1.

The Cr^{III} ions in the absorption spectrum of the ternary phase in $HClO_4$ solution absorb at higher wavenumbers (17.40 and 24.40×10^3 cm^{-1}; curve 4 of Figure 2) than the corresponding bands in the reflectance spectrum of β-$CaCr^{III}{}_2O_4$ (16.12×10^3 and 21.74×10^3 cm^{-1}; curve 3 of Figure 2). This blue shift, in agreement with the spectral finding[47] reporting the spectra of Cr^{III} ions in both MgO crystals and the hexahydrate $[Cr(H_2O)_6]^{3+}$ ion (see Table II), may be ascribed[47] to the larger magnitude of the cubic field strength parameter Dq for the octahedrally coordinated Cr^{III} ion in crystals than in the hexahydrate ion having the same coordination; e.g., Dq values of the Cr^{III} ion in MgO crystals and in hexahydrate ions are 2270 and 1760 cm^{-1}, respectively.

(c) Spectral Assignment. The bands observed in the different spectra obtained were interpreted on the basis of the electronic spectra of d^0 [28,40,42,48] and d^1 [28,48] tetraoxo species and d^3 octahedral complexes.[49]

(1) Ternary Phase. It is reasonable to identify the 16.00×10^3 cm^{-1} band, observed in the visible region of the diffuse spectrum of this phase (Figure 2, curve 2 and Table II), as the crystal field band $e \rightarrow t_2$ ($d \rightarrow d$ excitation)[28] and the maximum at 27.78×10^3 cm^{-1} in the UV region as the first charge-transfer band: $t_1 \rightarrow 2e$.[48]

(2) Calcium Chromate. It seems likely that the 27.03×10^3 cm^{-1} intense band observed in the UV region of the reflectance spectrum of $CaCr^{VI}O_4$ (Figure 2, curve 1) is the first electron-transfer band: $(\pi)t_1 \rightarrow d(e)$ $(^1A_1 \rightarrow {}^1T_2)$.[28]

The results in Figure 2 and Table II clearly show that the energy of the first charge-transfer band in the spectrum of the ternary phase (27.78×10^3 cm^{-1}) is higher than the energy (27.03×10^3 cm^{-1}) of the same band in the spectrum of $CaCr^{VI}O_4$; i.e., the first charge-transfer band moves to lower energy as the chromium valence is increased. This is in excellent agreement with the published spectral analyses on d^0 and d^1 systems of tetrahedral metal oxyanions.[48]

(3) β-Monocalcium Chromite. It seems reasonable to assign the bands observed in the diffuse-reflectance spectrum of β-$CaCr^{III}{}_2O_4$ at 16.12×10^3 and 21.74×10^3 cm^{-1} as well as in the optical spectrum of 3×10^{-2} M solution of the ternary phase in 4 N $HClO_4$ at 17.40×10^3 and 24.40×10^3 cm^{-1} (Figure 2, curves 3 and 4) as due to the spin-allowed transitions $^4A_2 \rightarrow {}^4T_2$ and $^4A_2 \rightarrow {}^4T_1$, respectively.[49] These transitions can be ascribed to the Cr^{III} ion in the octahedral crystal field.[49]

(C) Electron Spin Resonance (ESR) Spectroscopy. (1) Calcium Chromate. No ESR signal was observed for this phase. This is expected as Cr^{VI} has a $3d^0$ configuration with no unpaired electron spins.

(2) β-Monocalcium Chromite. The spectrum of polycrystalline β-$CaCr^{III}{}_2O_4$ was observed to be a broad line of approximately 700-G peak–peak line width centered around $g \approx 2$. The resonance absorption detected at room temperature for this phase, having the Cr^{III} ion in an octahedral coordination with a $3d^3$ configuration and three unpaired electrons as well as a total $S = {}^3/_2$, is similar to that reported at room temperature for polycrystalline Cr_2O_3 [50] and various Cr^{III}-containing compounds.[51]

(3) Ternary Phase. No ESR signal was detected in the spectrum of this phase over the magnetic field range 440–5400 G at room temperature. The absence of any ESR signal in the spectrum of this phase *confirms the absence of* Cr^{III} in the composition of this phase *in the solid state*.

That no ESR signal was observed for Cr^{V} at room temperature, although it has a $3d^1$ configuration with one unpaired electron, is expected behavior for such ions in tetrahedral coordination.[22,52] Cr^{V} has tetrahedral symmetry and there are excited states close to the ground state. This together with a dynamic Jahn–Teller effect causes a short spin–lattice relaxation time, and broad absorption lines are *only* detectable at temperatures well below 80 K.[52,53] Also a strong temperature-dependent ESR absorption for Cr^{V} in tetrahedral coordination has been reported several times; e.g., the strong resonance of $Cr^{V}O_4^{3-}$ tetraoxoanion in alkaline solutions, detected at 20 K, was no longer observable at 90 K[22] and the well-resolved spectra for chlorospodiosite doped with the $Cr^{V}O_4^{3-}$ tetraoxoanion have *only* been observed at 77 K.[24,53]

Therefore, the study of the ESR spectrum of the ternary phase at temperatures between 4 and 77 K, which are not handy to us at the present time, is of great scientific interest.

Conclusions

The spectral results obtained confirm the absence of Cr^{III} in the composition of the solid ternary phase and strongly suggest the existence of the tetraoxoanion $Cr^{V}O_4^{3-}$. Hence, this phase is described *in the solid state* by the tricalcium orthochromate formula, $Ca_3(Cr^{V}O_4)_2$, rather than the chromate chromite formula, $Ca_9(Cr^{VI}{}_4Cr^{III}{}_2)O_{24}$. The latter formula, accepted until now, describes the composition of the ternary phase *only* in acid solutions, where Cr^{V} disproportionates into Cr^{VI} and Cr^{III}.

IR spectroscopy gives evidence for a significant distortion of the tetraoxo species $Cr^{V}O_4^{3-}$ from T_d to $\leq C_{2v}$ site symmetry. It also reveals a decrease in the Cr–O stretching frequency with the decrease in chromium valence.

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Diffuse-reflectance spectroscopy shows a decrease in the energy of the first charge-transfer band ($t_1 \rightarrow 2e$ at 27.78 × 10^3 cm^{-1} for $Cr^{V}O_4^{3-}$ and $(\pi)t_1 \rightarrow d(e)$ ($^1A_1 \rightarrow {}^1T_2$) at 27.03 × 10^3 cm^{-1} for $Cr^{VI}O_4^{2-}$) as the valency of chromium is increased.

The absorption maxima of the octahedrally coordinated Cr^{III} ion, corresponding to the spin-allowed transitions $^4A_2 \rightarrow {}^4T_2$ and $^4A_2 \rightarrow {}^4T_1$, occur in acid solution at higher wavenumbers (17.40 × 10^3 and 24.40 × 10^3 cm^{-1}, respectively) than in crystals of β-$CaCr^{III}{}_2O_4$ (16.12 × 10^3 and 21.74 × 10^3 cm^{-1}, respectively).

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Contribution from Union Carbide Corporation, South Charleston, West Virginia 25303,
and Molecular Structure Corporation, College Station, Texas 77840

$[Cs_9(18\text{-crown-6})_{14}]^{9+}[Rh_{22}(CO)_{35}H_x]^{5-}[Rh_{22}(CO)_{35}H_{x+1}]^{4-}$. Synthesis, Structure, and Reactivity of a Rhodium Carbonyl Cluster with Body-Centered and Cubic Arrangement of Metal Atoms

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The reaction of $Rh(CO)_2acac$ with $CsPhCO_2$ in 18-crown-6 solvent results in the formation of high-nuclearity rhodium clusters containing 15 or more metal atoms per cluster. The isolation of $[Cs_9(18\text{-crown-6})_{14}]^{9+}[Rh_{22}(CO)_{35}H_x]^{5-}[Rh_{22}(CO)_{35}H_{x+1}]^{4-}$ has been carried out after 15–17 h at 150–155 °C. This cluster is the largest discrete aggregate of metal atoms reported to date. The complex has been characterized via a complete three-dimensional X-ray diffraction study. It crystallizes in the monoclinic *Cm* space group with a = 76.779 (30) Å, b = 15.450 (9) Å, c = 15.741 (5) Å, β = 95.58 (3)°, V = 18463 Å^3, and ρ(calcd) = 2.058 g cm^{-3} for Z = 2. Diffraction data were collected at −110 °C with an Enraf-Nonius CAD 4 automated diffractometer and graphite-monochromatized Mo Kα radiation. The structure was solved by direct methods and refined by difference-Fourier and least-squares techniques. All nonhydrogen atoms have been located and refined; the poor crystal properties and probably some disorder of the crown ether molecules resulted in final discrepancy indices of R_F = 9.8% and R_{wF} = 12.2% for 4390 independent reflections in the range of 0.8° ≤ 2θ ≤ 45°. The structures of two types of cation present in the cell, $[Cs(C_{12}H_{24}O_6)]^+$ and $[Cs_2(C_{12}H_{24}O_6)_3]^{2+}$, represent new species. The latter one is an unprecedented example of a "triple-decker" crown–alkali cation complex. The average cesium–oxygen bonding distances are in the ranges 3.35–3.43 Å for the former species and 3.59–4.02 Å for the latter one. The rhodium cluster consists of 12 rhodium atoms occupying the corners of two distorted rectangular prisms that share a common face. One capping atom is sitting on each of the two opposite basal faces, while six other atoms are capping three couples of vicinal prismatic faces. One of these couples is stereochemically unique, resembling the structure of $M_2(CO)_8$ (M = Co, Rh). The two remaining rhodium atoms are encapsulated in the center of the cluster cavities. Rhodium–rhodium contacts are 2.62–3.11 and 3.41–3.87 Å for bonding and nonbonding contacts, respectively, while longer contacts of up to 4.70 Å are also present. The shortest interatomic distance of this type reported in clusters, 2.49 Å, is found between the two encapsulated atoms. There are 14 terminal, 17 edge-bridge, 2 face-bridge, and 2 semibridge carbonyls. Average distances for Rh–C and C–O are 1.81 and 1.18 Å for the first group, 2.00 and 1.19 Å for the second, 1.85, 2.15 and 1.27 Å for the third, and 1.76, 2.54 and 1.27 Å for the fourth. The anion reacts with acids and bases showing Brønsted behavior. It also reacts with carbon monoxide (1 atm, ambient temperature), probably generating two $[Rh_{15}(CO)_{27}]^{3-}$ ions plus one $[Rh_{14}(CO)_{25}H]^{3-}$. It is proposed the cluster could be formed by condensation of $[Rh_{15}(CO)_{27}]^{3-}$ with $[Rh_7(CO)_{16}]^{3-}$ or a cluster derived from it. The ^{13}C NMR spectrum of the anion shows a resonance at 211.5 ppm. The packing of rhodium atoms in the cluster corresponds to body-cubic-centered and cubic-close-packed arrangements in the outer and inner sections, respectively, with other structural characteristics indicating that the anion could model the changes expected for bcc → ccp interconversion.

Introduction

Transition metal clusters have attracted increasing attention either as potential catalysts[1,2] or as species containing new bonding modes for organic and inorganic substrates.[1,3] Their role as potential useful models for a wide range of surface phenomena[4] has also been described. In fact, clusters have been found which model the packing of atoms present in their respective metallic elements, e.g., rhodium and $[Rh_{13}(CO)_{24}H_3]^{2-}$.[4] Other rhodium carbonyl clusters, $[Rh_{14}(CO)_{25}]^{4-}$ and $[Rh_{15}(CO)_{27}]^{3-}$, have also been proposed as suitable models of the structural rearrangement occurring in some surface.[5] A limitation of the study of cluster–surface analogies is the relatively small number of metal atoms present in a cluster[4,6] when compared with even the smallest crystallites. Thus, a main objective in the studies of transition

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