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## Spectral Properties of Chromium(III) Complexes with Some Amino Acids

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Series of Cr(III) complexes of some amino acids have been prepared. In these compounds, characterized by elemental analysis, diffuse reflectance and IR spectroscopy, the ligands are present as neutral molecules or bidentate anions, the donor atoms are nitrogen and oxygen. From the wavenumber of the *d*—*d* bands some spectrochemical, Racah, as well as angular overlap parameters have been calculated. The calculated parameters were compared with theoretical ones.

The interactions of such biologically important ligands as amino acids with Cr(III) ion have been a subject of great interest in recent years because of their activity in glucose metabolism [1, 2]. The electronic structure of Cr(III) complexes with amino acids was discussed in many experimental and theoretical papers [3—11]. Most of the data are available from the measurements of UV VIS spectra, IR spectra, and electron paramagnetic resonance (EPR) as well as magnetic susceptibilities. In majority of the papers no quantitative interpretation of the spectral properties of Cr(III) complexes has been reported. In this work we have studied the experimental spectra of some Cr(III) complexes with glutamic and anthranilic acids, tryptophan, serine, valine, methionine, histidine, and cysteine.

The spectra of Cr(III) complexes with amino acids have been theoretically studied using a crystal field model and an angular overlap model of Kurzak [12, 13].

Using DAFP program with the Davidson—Fletcher—Powell optimization algorithm to the resolution of electronic absorption spectra, the spectrochemical and Racah B, C parameters were calculated.

## EXPERIMENTAL

The measurements of diffuse reflectance spectra were carried out on a Hitachi 356 spectrophotometer in Li<sub>2</sub>CO<sub>3</sub> matrix at  $\lambda = 200$ —850 nm at room temperature. IR spectra were measured in KBr pellets at  $\tilde{\nu} = 400$ —4000 cm<sup>-1</sup>.

**Table 1.** Elemental Analysis of the Prepared Compounds

Compound	$w_i(\text{found})/\%$				
	C	H	N	Cl	Cr
Cr(ant) <sub>3</sub> · H <sub>2</sub> O	52.74	4.18	8.78	—	10.88
	50.33	4.40	8.39	—	10.89
Cr(val) <sub>3</sub> · H <sub>2</sub> O · KCl	35.26	6.66	8.23	6.95	10.19
	34.42	7.05	8.59	6.61	10.10
Cr <sub>2</sub> (tryp) <sub>4</sub> Cl <sub>2</sub> · 2H <sub>2</sub> O	51.41	5.06	10.91	6.91	10.13
	50.60	5.12	10.60	8.03	7.89
Cr <sub>2</sub> (glu) <sub>3</sub> (OH) <sub>2</sub> · 2H <sub>2</sub> O · KCl	26.25	4.23	6.13	5.18	13.00
	25.52	4.12	5.88	4.83	12.40
K[Cr(cys) <sub>2</sub> ] · 4H <sub>2</sub> O	18.05	4.51	7.02	—	13.03
	17.10	3.72	7.40	—	10.09
Cr(ser) <sub>3</sub> Cl <sub>3</sub> · H <sub>2</sub> O · 3KCl	17.84	3.30	6.94	17.59	8.59
	18.30	3.80	7.00	16.65	7.19
Cr(his) <sub>3</sub> Cl <sub>3</sub> · 3H <sub>2</sub> O	32.02	4.45	18.68	15.79	7.71
	32.44	4.75	18.31	15.25	7.37
Cr <sub>2</sub> (met) <sub>4</sub> Cl <sub>2</sub> · 2H <sub>2</sub> O · KCl	26.29	4.82	6.13	15.55	11.39
	23.42	4.63	6.50	16.00	12.14

## Preparation of Compounds

10 cm<sup>3</sup> of water and 2 cm<sup>3</sup> of ethanol solution containing 0.005 mol of CrCl<sub>3</sub> · 6H<sub>2</sub>O (green) and 0.015 mol of amino acid were heated on a water bath. Then the solution was concentrated to one half of its volume. The pale green compound with anthranilic acid was precipitated from the hot solution. The complexes with other amino acids were formed after adding the KOH solution and adjusting pH to 8.0 and cooling the reaction mixture. Then the precipitates were washed several times with the mixture of water and ethanol or methanol. The results of elemental analysis are given in Table 1.

## RESULTS AND DISCUSSION

The analytical data of these compounds are reported in Table 1. The complexes obtained are all crystalline and intensely coloured. The electron reflectance spectra of prepared complexes are typical for Cr(III) compounds in a regular octahedral ligands field. Two distinct shoulders corresponding to the

spin-allowed  ${}^4A_{2g} \rightarrow {}^4T_{2g}$  (band I) and  ${}^4A_{2g} \rightarrow {}^4T_{1g}$  (band II) transitions should be observed. Next two or only one weak shoulder for the studied compounds, due to the spin-forbidden transitions  ${}^4A_{2g} \rightarrow {}^2T_{2g}$  and  ${}^4A_{2g} \rightarrow {}^2T_{1g}$  (quartet—doublet) within the visible range are observed. The first electron transitions (I and II band) are connected with a change of the Cr(III) ion configuration  $t_{2g}^3 \rightarrow t_{2g}^2 e_g^1$ , the second ones with a change of multiplication without changes of configuration. The wavenumbers of the above-mentioned four transitions, derived from the experimental spectra, are presented in Table 2.

For the Cr(III) complexes of octahedral coordinative configuration the energy of the first quartet—quartet absorption gives directly the crystal field parameter 10 Dq. From the equations expressing energy of band II and spin-forbidden electron transition energy [14]  $B_{35}$ ,  $B_{55}$ , and C Racah parameters should be calculated. The 10 Dq values of the prepared complexes are very close to the 10 Dq values of the typical octahedral Cr(III) complexes except Cr(ant)<sub>3</sub> · H<sub>2</sub>O as well as Cr(his)<sub>3</sub>Cl<sub>3</sub> · H<sub>2</sub>O [15]. These complexes present larger differences in consequence of the tetragonal distortion.

**Table 2.** Electronic Absorption Spectra of Cr(III) Complexes

Compound	Electron transitions $\tilde{\nu}/\text{cm}^{-1}$			
	${}^4A_{2g} \rightarrow {}^4T_{2g}$	${}^4A_{2g} \rightarrow {}^4T_{1g}$	${}^4A_{2g} \rightarrow {}^2T_{1g}$	${}^4A_{2g} \rightarrow {}^2T_{2g}$
Cr(ant) <sub>3</sub> · H <sub>2</sub> O	17 241	28 735	14 925	
Cr(val) <sub>3</sub> · H <sub>2</sub> O · KCl	18 587	25 510	14 577	
Cr <sub>2</sub> (tryp) <sub>4</sub> Cl <sub>2</sub> · 2H <sub>2</sub> O	18 348	26 809	14 285	25 641
Cr <sub>2</sub> (glu) <sub>3</sub> (OH) <sub>2</sub> · 2H <sub>2</sub> O · KCl	17 795	24 271	14 706	25 316
K[Cr(cys) <sub>2</sub> ] · 4H <sub>2</sub> O	18 248	25 188		
Cr(ser) <sub>3</sub> Cl <sub>3</sub> · H <sub>2</sub> O · 3KCl	18 587	26 178	14 492	
Cr(his) <sub>3</sub> Cl <sub>3</sub> · 3H <sub>2</sub> O	20 161	27 777	14 493	
Cr <sub>2</sub> (met) <sub>4</sub> Cl <sub>2</sub> · 2H <sub>2</sub> O · KCl	18 315	25 510	14 492	26 315

All values of Racah parameters have confirmed the strong metal—ligand interactions.

Having the above parameters, the nephelauxetic coefficients  $\beta_{35}$ ,  $\beta_{55}$  can be calculated from the relations

$$\beta_{35} = B_{35}/B_0 \text{ and } \beta_{55} = B_{55}/B_0$$

where  $B_0 = 920 \text{ cm}^{-1}$ .

From the relation

$$\beta_{35} = \eta^2 \beta_{55}$$

the  $\eta^2$  covalency parameter can be calculated.

The calculated 10 Dq,  $B_{35}$ ,  $B_{55}$ ,  $C$ ,  $\beta_{35}$ ,  $\beta_{55}$ ,  $\eta^2$  values are presented in Table 3. The covalent metal—

than  $\beta_{55}$ , so the covalent bond  $\sigma$  participates in the Cr—L bond in great part. However,  $\beta_{35}$  parameter is smaller than  $\beta_{55}$  of  $\text{Cr}(\text{ant})_3 \cdot \text{H}_2\text{O}$  because of great  $\pi$  bond in the Cr—L bond.

The parameters  $f$  (part of the ligand in 10 Dq) enable to qualify amino acids as ligands with regard to the strength of the ligand field in obtained complexes. Assuming  $f = 1$  for the complex of anthranilic acid in which carboxylate oxygen atoms are donor atoms,  $f$  parameters for the left amino acids confirm spectrochemical series. Using the diffuse reflectance spectra and studied above data, the spin-orbit coupling constants  $\xi$  are also calculated (Table 3). Their values decrease in consequence of the formation of the M—L bond. The experimental reflectance spectra are given in Figs. 1—8.

**Table 3.** Calculated Parameters for Obtained Complexes

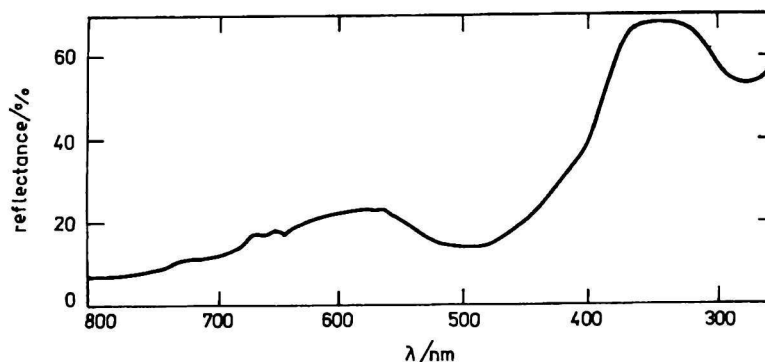
Compound	10 Dq/cm <sup>-1</sup>	$B_{55}$ /cm <sup>-1</sup>	$B_{35}$ /cm <sup>-1</sup>	$C$ /cm <sup>-1</sup>	$\beta_{35}$	$\beta_{55}$	$f$	$\eta^2$	$\xi$
$\text{Cr}(\text{ant})_3 \cdot \text{H}_2\text{O}$	14 241	710.7	957.8	2842.9	—	0.774	1	—	95.96
$\text{Cr}(\text{val})_3 \cdot \text{H}_2\text{O} \text{ KCl}$	18 587	694.1	576.9	3128.2	0.628	0.756	1.078	0.831	57.78
$\text{Cr}_2(\text{tryp})_4\text{Cl}_2 \cdot 2\text{H}_2\text{O}$	18 348	732.6	705.1	3012.9	0.768	0.798	1.064	0.962	70.66
$\text{Cr}_2(\text{glu})_3(\text{OH})_2 \cdot 2\text{H}_2\text{O} \text{ KCl}$	17 793	711.8	539.8	2847.2	0.588	0.774	1.032	0.708	54.09
$\text{K}[\text{Cr}(\text{cys})_2] \cdot 4\text{H}_2\text{O}$	18 248	—	578.3	2313.2	0.629	—	1.058	—	57.87
$\text{Cr}(\text{ser})_3\text{Cl}_3 \cdot \text{H}_2\text{O} \text{ 3KCl}$	18 248	690.1	632.6	2837.9	0.689	0.750	1.080	0.919	63.39
$\text{Cr}(\text{his})_3\text{Cl}_3 \cdot 3\text{H}_2\text{O}$	20 161	690.1	634.7	2760.4	0.691	0.750	1.170	0.921	63.57
$\text{Cr}_2(\text{met})_4\text{Cl}_2 \cdot 2\text{H}_2\text{O} \text{ KCl}$	18 315	720.9	599.6	2883.9	0.784	0.784	1.062	0.832	59.98

ligand bond in different complexes of the same metal ion is characterized by the nephelauxetic coefficient. It is less when ligand orbital overlaps on metal orbital in great part. The parameters  $\beta_{35}$  and  $\beta_{55}$  form the nephelauxetic series of amino acids as ligands. Their values indicate that the Cr—ligand (Cr—L) bonds are of considerable covalent character. Moreover, the donor atom (N or O) electrons can be situated as close to Cr(III) orbitals as electron repulsion parameters  $B_{35}$  or  $B_{55}$  are smaller than for free metal ion  $B_0$ .

Simultaneously the  $\eta^2$  values for all obtained complexes are above 0.5, which expresses a large participation of covalent interaction in the metal—ligand bond. In the most obtained compounds  $\beta_{35}$  is greater

Gaussian analysis of these spectra, the comparison of the experimental and calculated transition energies together with their assignments for these complexes have been made. The band assignments are based on fitting of the resolved band maxima with calculated transition energies using  $d^3$  matrix elements in conjunction with the supposed octahedral symmetry. The values of the experimental and theoretical parameters for prepared complexes are the same. The results are collected in Table 3.

The coordination position may be determined from the analysis of the IR spectra (Table 4). The appearance of the bands corresponding to symmetric and antisymmetric vibrations of the carboxylic group as



**Fig. 1.** Reflectance spectra of  $\text{Cr}(\text{ant})_3 \cdot \text{H}_2\text{O}$ .

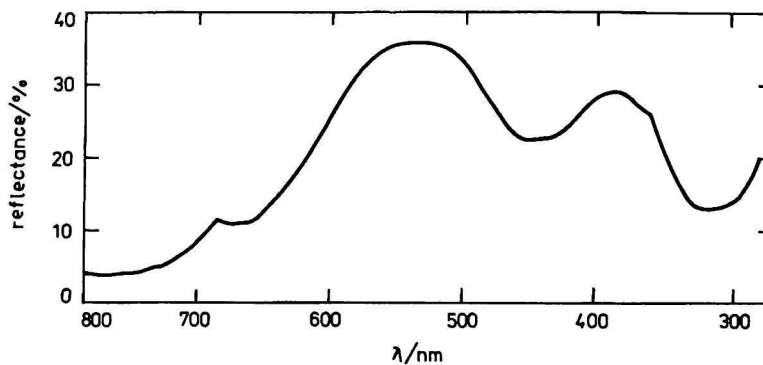


Fig. 2. Reflectance spectra of  $\text{Cr}(\text{val})_3 \cdot \text{H}_2\text{O} \text{ KCl}$ .

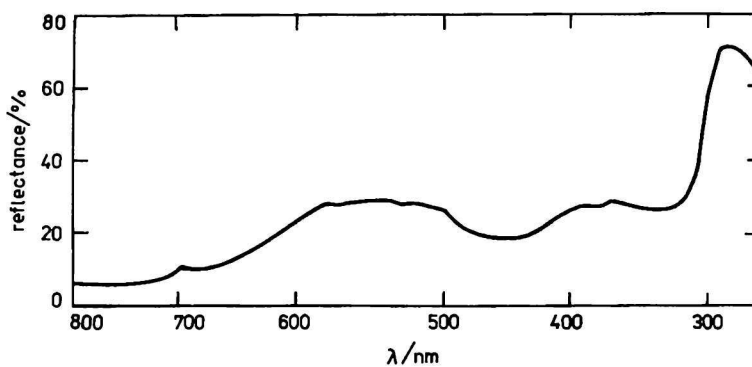


Fig. 3. Reflectance spectra of  $\text{Cr}_2(\text{tryp})_4\text{Cl}_2 \cdot 2\text{H}_2\text{O}$ .

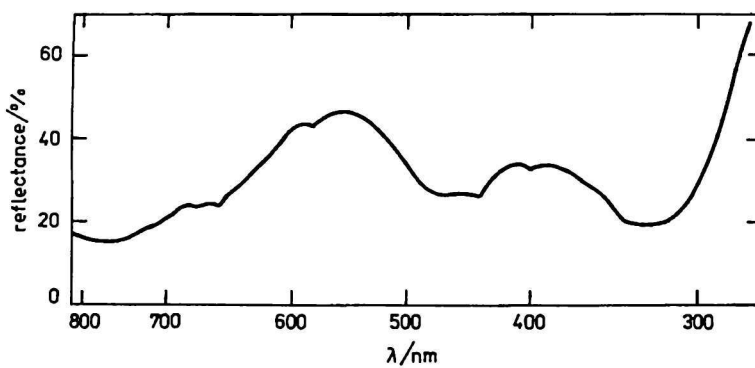


Fig. 4. Reflectance spectra of  $\text{Cr}_2(\text{glu})_3(\text{OH})_2 \cdot 2\text{H}_2\text{O} \text{ KCl}$ .

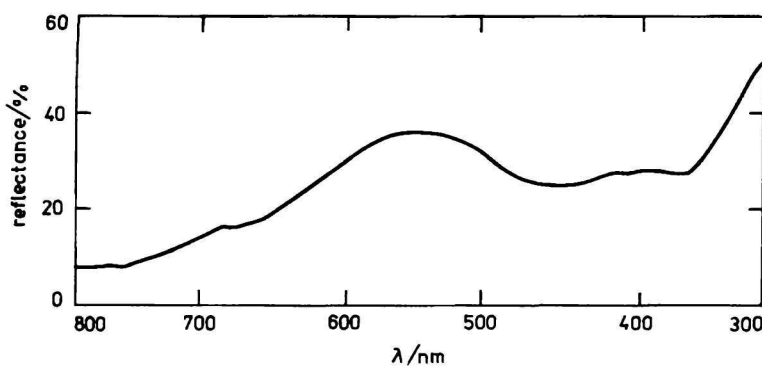
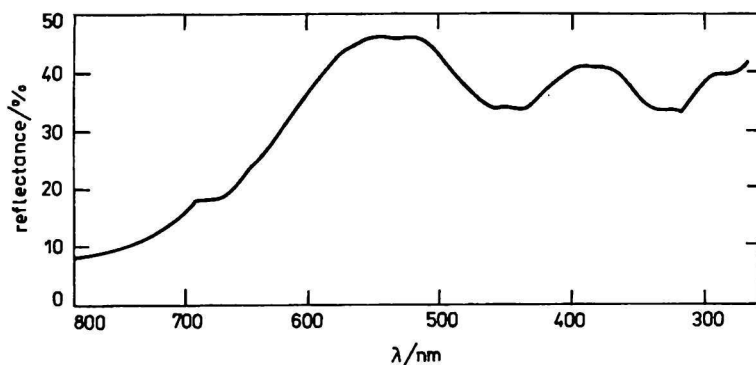
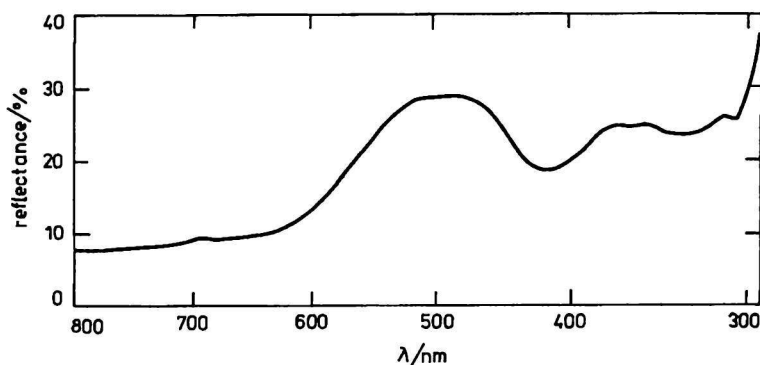
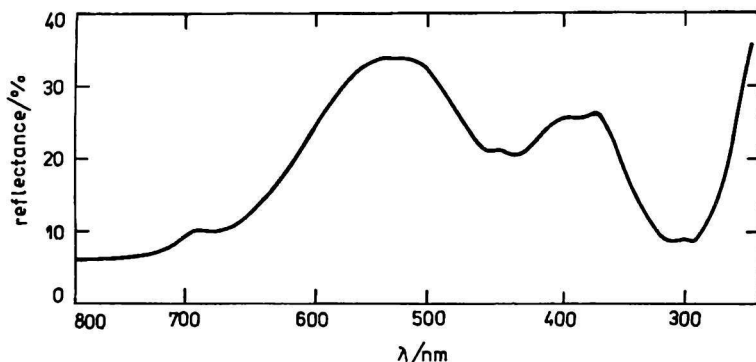


Fig. 5. Reflectance spectra of  $\text{K}[\text{Cr}(\text{cys})_2] \cdot 4\text{H}_2\text{O}$ .

Fig. 6. Reflectance spectra of  $\text{Cr}(\text{ser})_3\text{Cl}_3 \cdot \text{H}_2\text{O} \cdot 3\text{KCl}$ .Fig. 7. Reflectance spectra of  $\text{Cr}(\text{his})_3\text{Cl}_3 \cdot 3\text{H}_2\text{O}$ .Fig. 8. Reflectance spectra of  $\text{Cr}_2(\text{met})_4\text{Cl}_2 \cdot 2\text{H}_2\text{O} \cdot \text{KCl}$ .

well as the great differences between their frequencies suggest that oxygen is the donor atom. This bond is strong. The bands at  $\tilde{\nu} = 630 \text{ cm}^{-1}$  are interpreted as the vibrations of halogen bridges in the complexes with tryptophan and methionine. Similarly the bands at  $\tilde{\nu} = 550 \text{ cm}^{-1}$  are assigned to



The ligands amino acids are present as bidentate anions or neutral molecules. Nitrogen atoms of amino group and oxygen of carboxylic group are the do-

nor atoms (ligators) to the central metal Cr ion except  $\text{Cr}(\text{ant})_3 \cdot \text{H}_2\text{O}$ , where only oxygen is the donor atom as well as  $\text{Cr}(\text{his})_3\text{Cl}_3 \cdot 3\text{H}_2\text{O}$ , where histidine acts as neutral molecule. In all compounds the  $\sigma$  bonds are strong and covalent in great part. On the other hand, the  $\pi$  bonds also exist, particularly in the complexes with tryptophan, anthranilic and glutamic acids. The crystal field parameters of these complexes in our calculations suggested, in agreement with crystal structure, that the perturbations of the octahedron around Cr(III) ion are very weak.

Moreover, the  $\sigma$ - and  $\pi$ -bonding ability of amino acids is greater than that of water.

Table 4. Characteristic Frequencies of Ligands and Complexes

Compound	$\tilde{\nu}/\text{cm}^{-1}$		
	Ligand	Complex	Assignment
Cr(ant) <sub>3</sub> · H <sub>2</sub> O	3238	3250	$\nu(\text{NH}_2)$ s
	2921	2930	$\nu(\text{NH}_3^+)$
	1663	1630	$\nu_{\text{as}}(\text{C}=\text{O}), \nu_{\text{as}}(\text{OCO})$
	1370	1390	$\nu_{\text{s}}(\text{OCO})$
		580	$\nu(\text{Cr}-\text{O})$
	1035	1050	$\nu(\text{COO})$
	1072	1100	$\nu(\text{COO})$
Cr <sub>2</sub> (tryp) <sub>4</sub> Cl <sub>2</sub> · 2H <sub>2</sub> O	3404	3400	$\nu(\text{NH}_2)$ s
	2962	2930	$\nu(\text{NH}_3^+)$
	1664	1630	$\nu_{\text{as}}(\text{C}=\text{O}), \nu_{\text{as}}(\text{OCO})$
	1410	1400	$\nu_{\text{s}}(\text{OCO})$
	1068, 1096	1020, 1110	$\nu(\text{COO})$
		515	$\nu(\text{Cr}-\text{O})$
	600	$\nu \left( \begin{array}{c} \text{OH} \\ \diagdown \quad \diagup \\ \text{Cr} \quad \text{Cr} \\ \diagup \quad \diagdown \\ \text{OH} \end{array} \right)$	
Cr(his) <sub>3</sub> Cl <sub>3</sub> · 3H <sub>2</sub> O	3130	3120	$\nu(\text{NH}_2)$ s
	2859	2890	$\nu(\text{NH}_3^+)$
	1632	1620	$\nu_{\text{as}}(\text{C}=\text{O}), \nu_{\text{as}}(\text{OCO})$
	1355	1360	$\nu_{\text{s}}(\text{OCO})$
	1067, 1092	1030, 1080	$\nu(\text{COO})$
	500, 590	$\nu(\text{Cr}-\text{O})$	
Cr <sub>2</sub> (met) <sub>4</sub> Cl <sub>2</sub> · 2H <sub>2</sub> O · KCl	2915	2920	$\nu(\text{NH}_2)$ s
	1654	1630	$\nu_{\text{as}}(\text{C}=\text{O}), \nu_{\text{as}}(\text{OCO})$
	1341, 1315	1380, 1326	$\nu_{\text{s}}(\text{OCO})$
	1415	1440	$\nu_{\text{s}}(\text{OCO})$
	1081	1090	$\nu(\text{COO})$
	590	$\nu(\text{Cr}-\text{O})$	
Cr(val) <sub>3</sub> · H <sub>2</sub> O · KCl	1600	1646	$\nu_{\text{as}}(\text{C}=\text{O}), \nu_{\text{as}}(\text{OCO})$
	1420	1380	$\nu_{\text{s}}(\text{OCO})$
	1030, 1138	1020, 1140	$\nu(\text{COO})$
Cr(ser) <sub>3</sub> Cl <sub>3</sub> · H <sub>2</sub> O · 3KCl	1600	1647	$\nu_{\text{as}}(\text{C}=\text{O}), \nu_{\text{as}}(\text{OCO})$
	1467	1380	$\nu_{\text{s}}(\text{OCO})$

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