

Polyiodide Amide Complexes of Transition Metals: Structures and Raman Spectra

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Received May 22, 2008

Abstract—The Raman spectra of the polyiodide complexes of *d* elements with urea (Ur) and acetamide (AA), namely, $[\text{M}(\text{Ur})_6][\text{I}_3]_3$ ($\text{M} = \text{Cr}, \text{Fe}$), $\text{Co}(\text{Ur})_6[\text{I}_3]_2 \cdot 2\text{Ur}$, $[\text{Mn}(\text{Ur})_6][\text{I}_8]$, $[\text{Ni}(\text{AA})_6][\text{I}_3]_2$, $[\text{M}(\text{AA})_6][\text{I}_{10}]$ ($\text{M} = \text{Fe}, \text{Co}, \text{Cd}$), and $[\text{Co}(\text{AA})_4(\text{H}_2\text{O})_2][\text{I}_{12}]$, are studied. The structure of $[\text{Cr}(\text{Ur})_6][\text{I}_3]_3$ is studied. The crystals of $[\text{Cr}(\text{Ur})_6][\text{I}_3]_3$ are monoclinic: space group $C2/c$, $a = 15.260(5)$, $b = 11.941(3)$, $c = 20.506(6)$ Å, $\beta = 106.14(3)^\circ$, $Z = 4$, $V = 3589.4(18)$ Å³. The I–I bond length in the $\text{CdI}_2 \cdot 4\text{BA} \cdot 2\text{I}_2$ polyiodide complex amorphous to X-rays is estimated by a correlation between the I–I bond length and the frequency of vibrations of this bond in the Raman spectra.

DOI: 10.1134/S107032840902002X

INTRODUCTION

The structures of many polyiodides containing anions from I_3^- to I_{29}^{3-} [1], including a series of the polyiodide complexes of manganese, iron, cobalt, nickel, zinc, and cadmium with urea (Ur) and acetamide (AA), are presently studied [2–6]. The $[\text{Cr}(\text{Ur})_6]\text{I}_3$ compound is known for chromium [7] and analogous to the corresponding iron derivative [8] that reacts with iodine to form polyiodide $[\text{Fe}(\text{Ur})_6][\text{I}_3]_3$ [2]. It can be assumed that the chromium carbamide complex can produce an analogous polyiodide. The structures of chromium polyiodides were determined only for $[\text{Cr}(\text{NH}_3)_6](\text{I}_3)(\text{I}_4)$ and $[(\text{NH}_3)_3\text{Cr}(\text{OH})_3\text{Cr}(\text{NH}_3)_3](\text{I}_3)_2\text{I}$ [9].

Raman spectra together with X-ray diffraction analysis are very informative in investigation of polyiodides. When analyzing vibrational spectra, the polyiodide anions are considered as adducts of the $[(\text{I}^-)_{n-y} \cdot (\text{I}_3^-)_y \cdot (\text{I}_2)_{m-y}]$ type [10]. The Raman spectra can provide information on the structure of the components of these adducts, namely, triiodide ions and iodine molecules.

The purpose of this work is to find correlations between the I–I bond length and the frequency of stretching vibrations in the Raman spectra of the polyiodides. For this purpose, one should synthesize the chromium carbamide polyiodide complex, analyze the Raman spectra of the amide polyiodide complexes of *d* metals, and compare the spectral and structural characteristics of the compounds that make it possible to sug-

gest the structures of the polyiodides, whose X-ray diffraction study was impossible.

EXPERIMENTAL

Synthesis of hexacarbamidechromium(III) tris(triiodide) $[\text{Cr}(\text{Ur})\text{III}] [\text{Cr}(\text{Ur})_6][\text{I}_3]_3$ (I). Metallic chromium (0.52 g) was placed in concentrated hydroiodic acid containing iodine (10 ml), and carbamide (3.5 g) was added. Complex **I** was isolated from the reaction mixtures as shining plate-like black crystals. The product was filtered off and dried in a desiccator over calcium chloride to a constant weight for 5 h (70% yield). The composition of the compound was determined by X-ray diffraction analysis.

IR (cm⁻¹): 3427 $\nu_{\text{as}}(\text{NH}_2)$, 3327 $\nu_{\text{s}}(\text{NH}_2)$, 1630 $\nu(\text{C}=\text{O})$, 1545 $\delta(\text{NH}_2) + \nu(\text{C}=\text{O})$, 1493 $\nu_{\text{as}}(\text{CN})$, 1141 $\rho(\text{NH}_2)$, 1033 $\nu_{\text{s}}(\text{C}-\text{N})$, 751 $\delta(\text{NH}_2)$.

The other iodides studied in the present work were synthesized by described procedures [2–6].

X-ray diffraction analysis was carried out on an Enraf-Nonius CAD-4 automated diffractometer (MoK_α radiation, graphite monochromator, ω scan mode). The structure was solved by direct methods and refined by the full-matrix least-squares method in the anisotropic approximation for all non-hydrogen atoms (SHELX-97) [11]. Hydrogen atoms calculated geometrically were included in the refinement by the riding method. The crystallographic data, details of the X-ray diffraction experiment, and refinement parameters for the structure of compound **I** are given in Table 1. The bond lengths and bond angles are listed in Table 2. The IR spectrum

of compound **I** were measured on a Bruker EQUINOX 55/S single-beam spectrometer in a region of 400–4000 cm^{-1} (KBr pellets).

Raman spectra were excited by a line of 1.06 μm of a neodymium laser in the inverse scattering geometry. The laser radiation was focused onto a sample by a long-focus lens, and the power density on the sample did not exceed 5 W/cm^2 . The polycrystalline sample was placed in a closed quartz cell mounted on a three-coordinate stage movable in the micrometric scale. The scattered light was analyzed with an RFS 100/S Fourier–Raman spectrometer (Bruker) in which a germanium receiver cooled with liquid nitrogen was used as a detector. The scattered exciting light was suppressed with a unit of notch filters that cut the spectrum below than $\sim 50 \text{ cm}^{-1}$. Interferograms of the spectra were detected at a spectrometer spectral resolution of 2 cm^{-1} , and the accumulation time of an interferogram was 10 min (200 scans). The Fourier transform of the obtained interferograms was performed using the OPUS program.

RESULTS AND DISCUSSION

The IR spectroscopic data indicate the monodentate character of the urea molecules in compound **I** and their coordination through the oxygen atoms. The bands of stretching vibrations of the carbonyl groups are shifted to lower frequencies compared to their position in the spectrum of free carbamide (from 1686 and 1629 to 1630 and 1545 cm^{-1} , respectively). No bands at 1200 and 950 cm^{-1} , which serve as a criterion for the coordination of the carbamide molecules through the nitrogen atoms [12], are observed in the spectrum of complex **I**.

The structural units in crystal structure **I** are the $[\text{Cr}(\text{Ur})_6]^{3+}$ complex cations (in the 2 axis) and $[\text{I}_3]^-$ anions (Fig. 1). The chromium atom coordinates the oxygen atoms of six urea molecules at the vertices of

Table 1. Crystallographic data, details of X-ray diffraction experiment, and refinement parameters of the $[\text{Cr}(\text{Ur})_6][\text{I}_3]_3$ structure (**I**)

Parameter	Value
Empirical formula	$\text{C}_6\text{H}_{24}\text{CrI}_9\text{N}_{12}\text{O}_6$
FW	1554.47
Crystal system	Monoclinic
Space group	$C2/c$
a , Å	15.260(5)
b , Å	11.941(3)
c , Å	20.506(6)
β , deg	106.14(3)
Z	4
V , Å ³	3589.4(18)
T , K	293(2)
ρ_{calcd} , g/cm^3	2.877
θ_{max} , deg	27.00
μ_{Mo} , mm^{-1}	8.098
Number of reflections	3925
Number of independent reflections, $I \geq 2\sigma(I)$	3925
Number of refined parameters	155
$F(000)$	2772
R ($I \geq 2\sigma(I)$)	0.0455
R_w ($I \geq 2\sigma(I)$)	0.1480
R_{int}	0.0291
$\Delta\rho_{\text{max}}/\Delta\rho_{\text{min}}$, $e \text{ Å}^{-3}$	1.044/–1.013
Goodness-of-fit	1.484

the octahedron. In spite of a large scatter in individual values, the average C–O and C–N bond lengths are similar to analogous values in free urea (1.256 and 1.334 Å, respectively [13]).

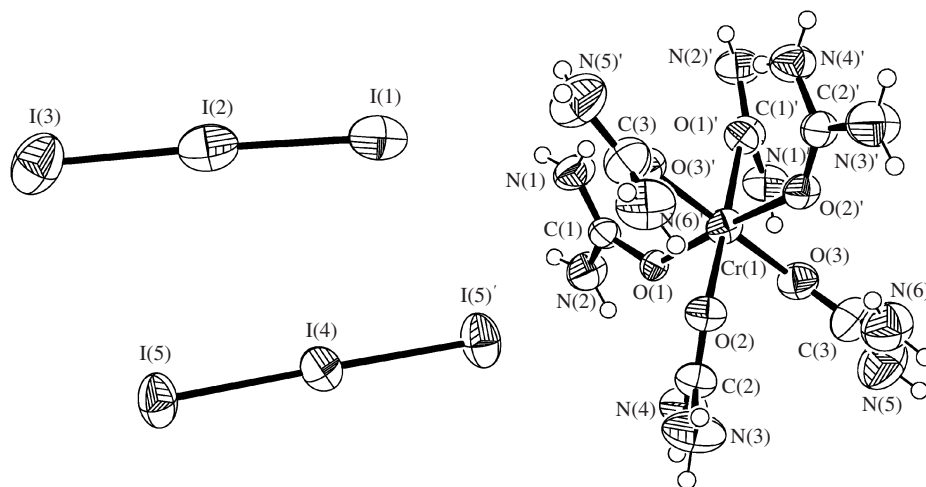


Fig. 1. Fragment of the $[\text{Cr}(\text{Ur})_6][\text{I}_3]_3$ structure.

Table 2. Bond lengths and bond angles in the $[\text{Cr}(\text{Ur})_6][\text{I}_3]_3$ structure*

Bond	d , Å	Angle	ω , deg
Cr(1)–O(1)	1.9771(15)	O(3) ^{#2} Cr(1)O(3)	175.90(14)
Cr(1)–O(2)	1.9686(17)	O(3)Cr(1)O(2) ^{#2}	91.34(9)
Cr(1)–O(3)	1.962(2)	O(3)Cr(1)O(2)	91.62(9)
I(1)–I(2)	2.8904(9)	O(2) ^{#2} Cr(1)O(2)	87.86(10)
I(2)–I(3)	2.9404(10)	O(3)Cr(1)O(1)	91.75(8)
I(4)–I(5)	2.9143(9)	O(2)Cr(1)O(1)	89.97(7)
C(1)–N(1)	1.303(3)	O(3)Cr(1)O(1) ^{#2}	85.41(8)
C(1)–O(1)	1.305(3)	O(2)Cr(1)O(1) ^{#2}	176.27(6)
C(1)–N(2)	1.314(4)	O(1)Cr(1)O(1) ^{#2}	92.36(9)
C(2)–O(2)	1.207(3)	I(1)I(2)I(3)	177.156(13)
C(2)–N(4)	1.342(3)	I(5) ^{#1} I(4)I(5)	177.904(14)
C(2)–N(3)	1.345(4)	N(1)C(1)O(1)	125.0(2)
C(3)–O(3)	1.257(4)	N(1)C(1)N(2)	123.9(2)
C(3)–N(6)	1.336(6)	O(1)C(1)N(2)	111.1(2)
C(3)–N(5)	1.376(5)	C(1)O(1)Cr(1)	130.53(14)
		O(2)C(2)N(4)	124.0(2)
		O(2)C(2)N(3)	119.4(2)
		N(4)C(2)N(3)	116.5(2)
		C(2)O(2)Cr(1)	134.29(16)
		O(3)C(3)N(6)	131.7(3)
		O(3)C(3)N(5)	117.3(4)
		N(6)C(3)N(5)	111.0(4)
		C(3)O(3)Cr(1)	129.5(2)

* Symmetry procedures: ^{#1} $-x, y, -z + 1/2$; ^{#2} $-x + 1, y, -z + 1/2$.

Table 3. Assignment of bands in the Raman spectra of the complexes of d metals with urea and acetamide containing triiodide ions

Compound	ν_1	ν_2	ν_3
I	116(100)	85(9)	
II	113(100)	93(11)	147(47)
III	112(100)	84(91)	135(18)
IV	117(100)	84(50)	

In crystal structure **I**, one (centrosymmetric) anion is isolated, and two others (in the general position) are nonsymmetric and bound to each other by the weak I...I contact (3.825 Å) to form short $[\text{I}_6]^{2-}$ chains. The structure consists of alternating layers formed by piles of the $[\text{I}_6]^{2-}$ chains and layers of columns of the alternating cations and symmetric triiodide ions. The layers are stabilized by hydrogen bonds.

Thus, structure **I** noticeably differs from the $[\text{Fe}(\text{Ur})_6][\text{I}_3]_3$ structure (**II**), where the triiodide anions are joined together by interionic contacts into infinite

zigzag chains oriented in such a way that they form hexahedral channels, and the piles of the complex cations are localized in these channels [2]. Unlike Fe(III) (d^5 electron configuration), for Cr(III) (d^3) the effect of stabilization by the octahedral ligand field is observed. This results in a greater rigidity of the octahedral chromium complex (**I**), and the latter cannot “tune” to the iodine sublattice so easily as iron complex **II** does. Therefore, structure **I** is layered rather than channel-like.

According to the selection rules, the centrosymmetric triiodide ion is characterized by one band in the Raman spectrum corresponding to the symmetric stretching vibrations (ν_1) and two bands in the IR spectrum attributed to the degenerate bending and asymmetric stretching vibrations (ν_2 and ν_3 , respectively). These bands are usually observed at 110, 50–70, and 130–140 cm^{-1} , respectively [1].

The Raman spectrum of complex **II** exhibits intense bands at 113 and 147 cm^{-1} (ν_1 and ν_3) and a very weak band at 93 cm^{-1} (ν_2). The appearance of the ν_2 and ν_3 vibrations, which are inactive in the Raman spectra of the centrosymmetric I_3^- ions, indicates a decrease in the symmetry of the triiodide ions in agreement with the X-ray diffraction data [2]. The Raman spectrum of complex **I** containing more symmetric triiodide ions exhibits an intense band at 116 cm^{-1} and a very weak band at 85 cm^{-1} (Table 3).

Isolated triiodide ions were observed in $[\text{M}(\text{Ur})_6][\text{I}_3]_2 \cdot 2\text{Ur}$ ($\text{M} = \text{Co}$ (**III**), Ni) [4] and $[\text{Ni}(\text{AA})_6][\text{I}_3]_2$ (**IV**) [6]. The spectra of these compounds contain intense bands of symmetric stretching vibrations of I_3^- at 112–117 cm^{-1} . In addition, they exhibit lower-intensity bands at 84 cm^{-1} assigned to bending vibrations of the triiodide ions and at 135 cm^{-1} (for **IV**) ascribed to asymmetric stretching vibrations of the triiodide ion. These bands indicate a decrease in the triiodide ion symmetry, which is confirmed by the X-ray diffraction data [4, 6].

An intense band at 116 cm^{-1} caused by the symmetric stretching vibrations of the coordinated triiodide ion (ν_1) is observed in the Raman spectrum of $[\text{Mn}(\text{Ur})_6][\text{I}_8]$. A weak band at 85 cm^{-1} can be attributed to the bending vibrations of the triiodide ion (ν_2) inactive in the Raman spectra of the centrosymmetric triiodide ion. The appearance of this band is due, most likely, to a decrease in the symmetry of $[\text{I}_3]^-$. The band at 168 cm^{-1} caused by the symmetric stretching vibrations of the iodine molecule is appreciably shifted toward lower frequencies compared to its position in the spectrum of crystalline iodine [1]. This indicates the coordination of I_2 in the composition of the octaiodide ion.

The structures of the $[\text{M}(\text{Ur})_6][\text{I}_8]$ isostructural compounds ($\text{M} = \text{Mn}, \text{Co}$ (**V**), Ni) were studied by X-ray diffraction analysis using the cobalt polyiodide com-

plex as an example [3]. In the complex anions, the central iodine molecule coordinates two nonsymmetric $[I_3]^-$ anions *trans*-oriented toward the I_2 complexing agent.

The Raman spectrum of $[Cd(AA)_6][I_{10}]$ (**VI**) exhibits two intense bands. The band at 117 cm^{-1} can be assigned to the symmetric stretching vibrations in the triiodide ion (ν_1), and that at 178 cm^{-1} is ascribed to the vibrations in the coordinated iodine molecule [1]. The same bands are observed in the Raman spectra of analogous iron and cobalt compounds. However, the spectra of the $[M(AA)_6][I_{10}]$ complexes ($M = Fe, Co$) contain weak bands at 84 cm^{-1} , which can be assigned to the bending vibrations of the triiodide ion (ν_2). Since these vibrations for the centrosymmetric ion are inactive in the Raman spectra, the appearance of them in the spectra of the iron and cobalt compounds indicate a decrease in the symmetry of the triiodide ion.

The structures of the $[M(AA)_6][I_{10}]$ isostructural complexes were studied by X-ray diffraction analysis for cadmium compound **VI** [5] in the crystals of which the alternating iodine molecules and symmetric triiodide ions form infinite serpiginous chains.

The structural units of the $[Co(AA)_4(H_2O)_2][I_{12}]$ (**VII**) crystals are the $[Co(AA)_4(H_2O)_2]^{2+}$ complex cations and $[I_{12}]^{2-}$ anions [6]. The $[I_{12}]^{2-}$ anion is built of the V-like pentaiodide ions, whose vertices are linked through the iodine molecule. For the V-like pentaiodide ion, the vibrational spectra should contain four bands of stretching vibrations (symmetric (ν_1 and ν_2) at 157 – 164 and 90 – 130 cm^{-1} and asymmetric (ν_6 and ν_7) at 50 – 70 and 130 – 140 cm^{-1} [14]) and five bands of bending vibrations. The Raman spectrum of compound **VII** exhibits bands at ~ 150 and 110 cm^{-1} , which can be attributed to the symmetric stretching vibrations of the I–I bonds in the I_5^- ion (ν_1 and ν_2).

The data obtained by Raman spectroscopy and X-ray diffraction analysis for compounds **I**–**VII** (Table 4) and published data on the polyiodides of other types [14] show a linear dependence of the frequency of symmetric stretching vibrations of the I–I bond in the free and coordinated iodine molecules and triiodide ions on the I–I bond length (Fig. 2). An analogous dependence was previously found for the iodine charge-transfer complexes [15]. This makes it possible to use the data of the Raman spectra of the polyiodide complexes for the estimation of interatomic distances in polyiodide anions when their structures cannot be determined by X-ray diffraction analysis.

The Raman spectrum of the benzamide polyiodide cadmium derivative amorphous to X-rays ($CdI_2 \cdot 4BA \cdot 2I_2$) exhibits bands at 113 and 158 cm^{-1} . The band at 113 cm^{-1} in the spectrum of $(BA)_2HI_3$ was assigned to vibrations of the triiodide ions forming infinite chains [16]. The same band in the spectrum of the cadmium-containing polyiodide confirms that the polyiodide complex contains similar chains. The band at

Table 4. Frequency of symmetric stretching vibrations (ν) in the Raman spectra and the I–I bond lengths (d) in the polyiodide complexes of transition metals with amides

Compound	ν, cm^{-1}	$d, \text{\AA}$	Literature
I	116	2.915	This work
II	113	2.936	[2]
III	117	2.925	[4]
IV	112	2.912	[6]
V	116	2.914	[3]
VI	168	2.752	[5]
	117	2.910	
	178	2.740	
VII	110	2.925	[6]

158 cm^{-1} is due to vibrations of the coordinated I_2 molecule. It can be asserted that the bond length in the coordinated iodine molecule is $\sim 2.785\text{ \AA}$ (a bond order of ~ 0.7).

Thus, the new $[Cr(Ur)_6][I_3]_3$ polyiodide was synthesized, studied by X-ray diffraction analysis, and characterized by Raman spectroscopy along with the earlier synthesized amide polyiodide complexes of transition metals. A correlation between the X-ray diffraction and Raman spectral data for the metal polyiodide complexes was shown.

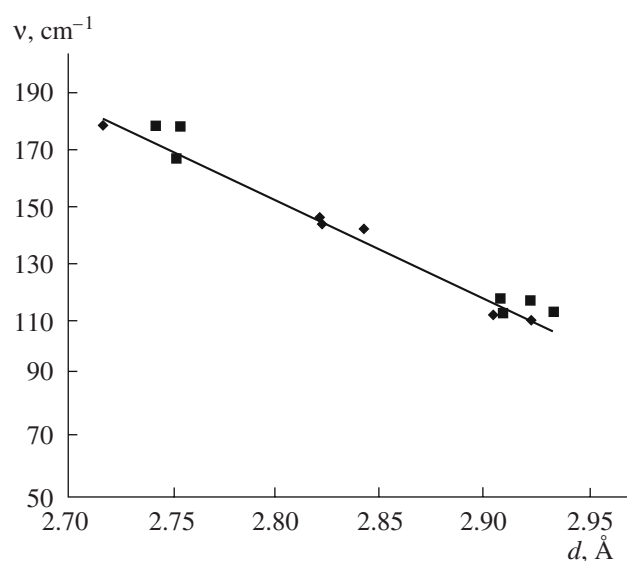


Fig. 2. Dependence of the frequency of symmetric stretching vibrations in the Raman spectra on the iodine–iodine bond length: (♦) published data [13] and (■) data of this work.

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