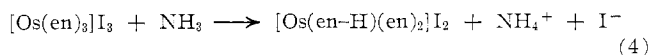


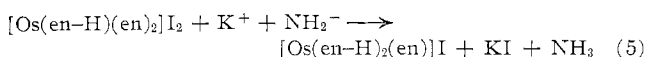
where (3) is quite slow relative to the rate of (2). An alternative explanation is suggested by the observation that when $[\text{Os}(\text{en})_3]\text{I}_3$ comes into contact with gaseous ammonia, it forms a yellow solid similar in appearance to the dihydrate. In liquid ammonia this changes to a white solid that dissolves to form a solution that has a red color characteristic of an ammonia solution of $[\text{Os}(\text{en-H})(\text{en})_2]\text{I}_2$. This, together with the pK_a of 5.1 for $[\text{Os}(\text{en})_3]\text{I}_3$, suggests that the NH_3 molecule is sufficiently basic to accomplish the deprotonation



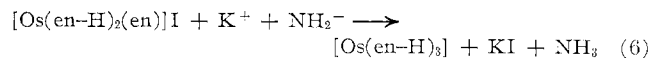
and that the K is consumed in reaction with NH_4^+ . That (4) is less probable than (2) and (3), however, follows from the well-known and essentially instantaneous reaction of ammonium ion with solutions of metals in ammonia.

The complex $[\text{Os}(\text{en-H})(\text{en})_2]\text{I}_2$ has the unusual property that, when ground in an inert atmosphere, it is converted to a product that gives an infrared spectrum identical with that for $[\text{Os}(\text{en-H})_2(\text{en})]\text{I}_2$ (*vide infra*) except for a sharp band at 675 cm^{-1} . This band can also be brought into the spectrum of $[\text{Os}(\text{en-H})_2(\text{en})]\text{I}_2$ by treatment with H_2 at 25° , and the band disappears when the sample is exposed to air.¹¹

Following reaction 1, further deprotonation was accomplished by the reactions



(11) The spectral data for $[\text{Os}(\text{en-H})_2(\text{en})]\text{I}_2$ in Table II are for a sample that was not ground but simply coated with Nujol and pressed between NaCl plates.



The products of these reactions together with the related species prepared by the method of Dwyer and Hogarth¹ afforded the first opportunity to compare the properties of deprotonated species involving different oxidation states of the central metal ion, particularly as evidenced by changes in the infrared spectra.

The tentative assignments of vibrational frequencies given in Table II were made on the basis of earlier studies^{12,13} and deuteration of $[\text{Os}(\text{en})_3]\text{I}_3 \cdot 2\text{H}_2\text{O}$ by rapid crystallization from 99.7% D_2O .¹⁴ The spectrum of $[\text{Os}(\text{en-H})(\text{en})_2]\text{I}_2$ is shown in Figure 1 as an example of the spectrum of a deprotonated Os-en complex in the $600\text{--}3400\text{ cm}^{-1}$ region even though the bands in the $\nu(\text{NH})$ and $\delta(\text{NH})$ regions are sharper than those in the spectra of the related complexes.¹⁵ Data in the $250\text{--}700\text{ cm}^{-1}$ are given in Table III only for complexes that gave useful spectra and are shown in Figure 2 to illustrate the marked similarity despite differences in oxidation state. Such shifts as are observed are comparable to those that result from successive deprotonation without change in oxidation state.¹⁶ Although it seems rather remarkable that change in the charge on the central metal ion should have so little effect on the metal-nitrogen stretching frequency, conclusions on this point should not be drawn until additional cases can be examined.

(12) D. B. Powell and N. Sheppard, *Spectrochim. Acta*, **17**, 68 (1961).

(13) G. W. Watt and D. S. Klett, *ibid.*, **20**, 1053 (1964).

(14) To avoid oxidation a large excess of NaI was used to hasten precipitation.

(15) The spectrum of $[\text{Os}(\text{en})_3]\text{I}_3 \cdot 2\text{H}_2\text{O}$ is illustrated elsewhere.⁸

(16) G. W. Watt and J. K. Crum, *J. Am. Chem. Soc.*, **87**, 5366 (1965).

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Spectra of Hexaimidazolidonechromium(III) and Tris(biuret)chromium(III) Perchlorates

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Two new compounds with structures similar to that of the hexaureachromium(III) complex have been studied. The visible spectra, in both emission and absorption, are compared with those of the urea complex, particularly with regard to the positions and intensities. With imidazolidone (ethyleneurea) and urea as ligands, the spectra are almost identical, but with biuret, which forms an oxygen-bonded chelate, the spin-allowed d-d bands are considerably shifted to the blue, while the spin-forbidden bands are virtually unchanged.

Introduction

In the course of an investigation of the low-temperature spectra of various chromium complexes, some new compounds of chromium(III) have been examined. In this work the syntheses, physical properties, and spectra (visible absorption and emission and infrared absorption) of hexaimidazolidonechromium(III) per-

chlorate and of tris(biuret)chromium(III) perchlorate are reported. It has been observed,¹ for the complex hexaureachromium(III), that the intercombination bands, *i.e.*, spin-forbidden transitions, have unusually high intensities in absorption and that both fluores-

(1) G. B. Porter and H. L. Schläfer, *Z. Physik. Chem. (Frankfurt)*, **37**, 109 (1963).

cence and phosphorescence are observed. The compounds discussed here are closely related to the urea complex; their spectra are therefore of considerable interest.

Experimental Section

Preparation of Hexaimidazolidonechromium(III) Perchlorate Dihydrate.—A solution of 9.2 g of chromium perchlorate hexahydrate and 10.4 g of 2-imidazolidone (mole ratio of 1:6) in water was evaporated almost to dryness. The green crystalline mass was then mixed with a little water, in which it is slightly soluble, filtered, and washed several times with small portions of warm water, cold water, and finally ethanol. It was dried at 60° for several hours; yield, 12.5 g (70%). *Anal.* Calcd for $[\text{Cr}(\text{C}_3\text{H}_5\text{N}_3\text{O}_2)_6](\text{ClO}_4)_3 \cdot 2\text{H}_2\text{O}$: C, 23.95; H, 4.43; N, 18.62; Cl, 11.75; Cr, 5.57. Found: C, 23.96; H, 4.73; N, 18.64; Cl, 11.95; Cr, 5.74. (Analyses were performed by A. Bernhardt, Mülheim.) The compound appeared as dark green, needle-shaped crystals, sparingly soluble in water, almost insoluble in ethanol, but freely soluble in dimethylformamide.

Preparation of Tris(biuret)chromium(III) Perchlorate.—A solution of 18.4 g of chromium perchlorate hexahydrate and 12.4 g of biuret (mole ratio 1:3) in 100 ml of water was heated on a water bath to give a clear solution. A violet crystalline mass left on evaporation of this solution to dryness was extracted with a small quantity of water, cooled, and filtered. This solution in turn was evaporated until most of the material had crystallized out. The solid was collected by filtration, washed three times with cold ethanol, and dried at 60°. The yield was 6 g (23%). *Anal.* Calcd for $[\text{Cr}(\text{C}_2\text{H}_5\text{N}_3\text{O}_2)_3](\text{ClO}_4)_3$: C, 10.93; H, 2.29; N, 19.11; Cl, 16.13; Cr, 7.88. Found: C, 10.98; H, 2.52; N, 19.4; Cl, 15.5; Cr, 7.84. The compound appeared as violet crystals, very soluble in water, ethanol, and acetone.

Absorption Spectra.—The spectra at room temperature were measured with a Cary 14 spectrophotometer in the following solvents: water and 95% ethanol for the biuret compound; water, dimethylformamide, and a 2:1 mixture of ethylene glycol and dimethylformamide for the imidazolidone compound. The solubility and stability of the compounds in these solvents dictated their choice.

Low-Temperature Spectra.—Both absorption and emission spectra at 77°K were recorded photographically on Kodak 1N plates with a Jarrell-Ash 0.5-m f 6.3 grating spectrograph (20 Å/mm in first order). The ethylene glycol-dimethylformamide mixture was used as solvent for the imidazolidone complex, and 95% ethanol was used for the other. Both solvents form glasses at low temperatures which do crack, but fortunately there is little loss of transparency.

The solutions were put in a low-temperature absorption cell of the type described by Wills and Waters² inside a cylindrical metal cryostat which could be evacuated and cooled with liquid nitrogen. There are three windows in the cryostat, two on opposite sides for absorption spectra and one additional at one side to allow front-surface illumination for emission spectra. A tungsten lamp provided a continuous spectrum for the absorption measurements. For emission spectra, a PEK X-75 xenon lamp was focused onto the sample through a copper sulfate solution and a Corning CS 470 blue filter (to eliminate red and infrared radiation from the exciting light). The luminescence was then focused onto the slit of the spectrograph through a Corning HR 2-61 red filter, almost completely complementary to the other filter combination.

Low-temperature absorption spectra were also measured with a cryostat designed to fit the sample compartment of a Cary 14 spectrophotometer. These measurements complement those done with the grating spectrograph, in that they simplify the intensity measurements, particularly of the broad, relatively intense bands.

Infrared Spectra.—Both Nujol mulls and potassium bromide

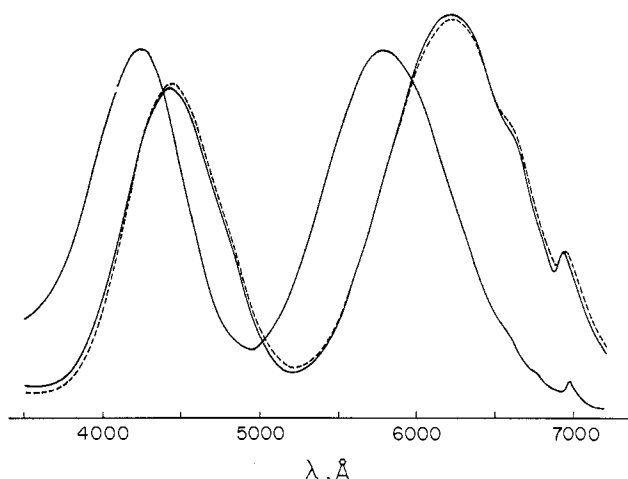


Figure 1.—Absorption spectra at room temperature of hexaurea-, hexaimidazolidone-, and tris(biuret)chromium(III) perchlorates.

pellets containing the complexes were examined in the region 650 to 4000 cm^{-1} with a Perkin-Elmer 21 spectrophotometer.

Results

The absorption spectra at room temperature are shown in Figure 1 for both of the complexes as well as that of the hexaureachromium(III) perchlorate for comparison. The spectra of the urea and the ethyleneurea (imidazolidone) complexes are, except for slightly higher extinction coefficients for the former, almost identical in all features. Although the narrow intercombination bands of all three compounds lie at about the same positions (see Table I), the broad bands of the biuret complex are shifted to higher energy relative to the other two complexes by about 1000 cm^{-1} . The latter compound was unstable in aqueous solution; the spectrum changed quite rapidly with time.

TABLE I
POSITIONS OF BAND MAXIMA (IN CM^{-1}) AND EXTINCTION COEFFICIENTS AT THE MAXIMA IN THE ROOM-TEMPERATURE ABSORPTION SPECTRA OF THE CHROMIUM(III) COMPLEXES OF UREA, 2-IMIDAZOLIDONE, AND BIURET

	Urea ^a	Imidazolidone ^a	Biuret ^b
${}^4\text{T}_{1g} \leftarrow {}^4\text{A}_{2g}$	22,570 (40.0)	22,570 (37.0)	23,530 (68.5)
${}^2\text{T}_{2g} \leftarrow {}^4\text{A}_{2g}$	20,490
${}^4\text{T}_{2g} \leftarrow {}^4\text{A}_{2g}$	16,130 (47.3)	16,130 (45.0)	17,240 (69.5)
${}^2\text{T}_{1g} \leftarrow {}^4\text{A}_{2g}$	15,050 (3.3)	15,040 (3.4)	15,220 (1.3)
${}^2\text{E}_g \leftarrow {}^4\text{A}_{2g}$	14,400 (5.1)	14,450 (5.5)	14,350 (3.5)

^a In water. ^b In 95% ethanol.

In the absorption spectra at low temperature, not only are the intercombination bands more clearly seen, but also the broad spin-allowed bands sharpen considerably, especially on the low-energy side. There are, however, no pronounced shifts in the absorption maxima. A comparison of the room-temperature and low-temperature absorption spectra of the biuret complex is given in Figure 2, where it will be noted that the integrated intensity of each band is not appreciably altered by the change in temperature.

The absorption and emission spectra at 77°K provide additional information about the spin-forbidden bands of lowest energy only. The relevant parts of

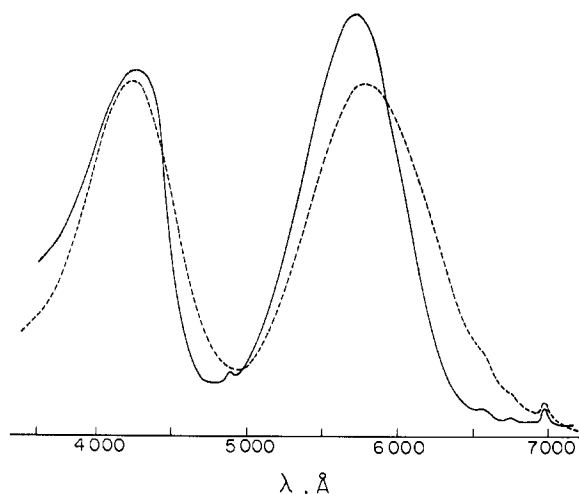


Figure 2.—Absorption spectra of tris(biuret)chromium(III) perchlorate at 25°C (-----) and at 77°K (———).

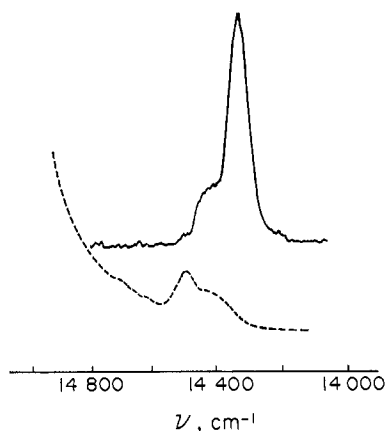


Figure 3.—High-resolution absorption (-----) and emission (———) spectra of hexaimidazolonechromium(III) perchlorate.

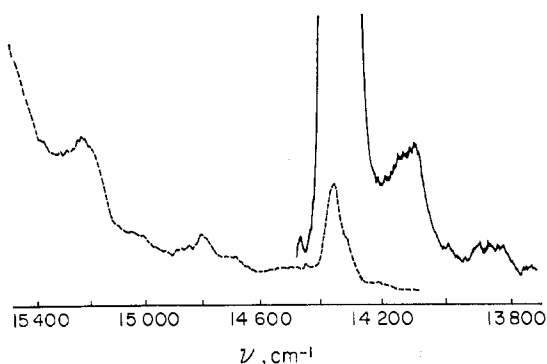


Figure 4.—High-resolution absorption (-----) and emission (———) spectra of tris(biuret)chromium(III) perchlorate.

the spectra are reproduced in Figure 3 (imidazolone complex) and in Figure 4 (biuret complex). A summary of the positions of the observed intercombination bands in the near-infrared region for the two compounds is given in Table II.

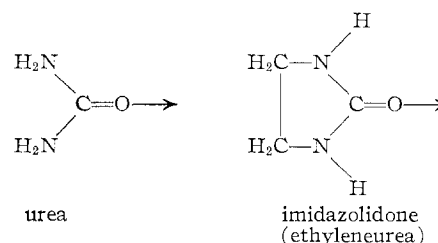
Discussion

The structure of the new complexes can best be inferred by comparison with the known structure of the hexaurea complex,³ in which six urea molecules are

TABLE II
POSITIONS OF THE INTERCOMBINATION BANDS IN THE ABSORPTION AND EMISSION SPECTRA OF THE CHROMIUM(III) COMPLEXES OF 2-IMIDAZOLIDONE AND BIURET AT 77°K

Imidazolidone	Biuret
Absorption	
14,490	14,800
~14,400	14,710
	14,360
Emission	
~14,400	14,370
14,340	14,310
	14,110
	13,860

coordinated to chromium through oxygen only. A comparison of the visible spectrum of the imidazolone complex with that of the urea complex provides convincing evidence that the coordination of the former is also *via* oxygen. The two ligands differ only at the nitrogen end of the molecules



The infrared spectra fully confirm this conclusion, not only for the urea complex⁴ but also for the imidazolone and the biuret complexes. The carbonyl frequency, which will be at about 1700 cm^{-1} in the ligand, increases when coordination is through nitrogen, as in the compound $\text{Pt}(\text{urea})_2\text{Cl}_2$, but decreases when coordination is through oxygen. For both the biuret and imidazolone complexes there is a shift to lower frequencies in this region when the complex ion spectrum is compared with that of the ligand: 1725 to 1685 and 1685 to 1660 cm^{-1} for biuret and 1660 to 1620 cm^{-1} for imidazolone.

The bands which appear in the visible absorption spectrum of tris(biuret)chromium(III) perchlorate are shifted relative to those of the hexaureachromium(III) complex. The broad spin-allowed bands: ${}^4\text{T}_{1g} \rightarrow {}^4\text{A}_{2g}$ and ${}^4\text{T}_{2g} \rightarrow {}^4\text{A}_{2g}$, in O_h symmetry, are displaced to higher energy by 960 and 1190 cm^{-1} , respectively, while the spin-forbidden bands are scarcely changed at all, perhaps 50 to 100 cm^{-1} for the transition ${}^2\text{E}_g \leftarrow {}^4\text{A}_{2g}$. It is, however, surprising that the ligand field strength does increase with chelation. The only other directly comparable case is that of the pair $[\text{Cr}(\text{NH}_3)_6]^{3+}$ and $[\text{Cr}(\text{en})_3]^{3+}$, in which the ${}^4\text{T}_{2g} \leftarrow {}^4\text{A}_{2g}$ transitions occur at 21,600 and 21,900 cm^{-1} , respectively, and the ${}^4\text{T}_{1g} \leftarrow {}^4\text{A}_{2g}$ transitions are both at 28,500 cm^{-1} .⁵ The effect is thus much greater for the urea-biuret pair than for the ammine-ethylenediamine pair.

(3) Y. Okaya, *et al.*, Abstracts, 4th International Congress of the International Union of Crystallography, Montreal, 1957, p. 69, quoted by F. A. Cotton in "Modern Coordination Chemistry," J. Lewis and R. G. Wilkins, Ed., Interscience Publishers, Inc., 1960, New York, N. Y., p. 389.

(4) R. B. Penland, S. Mizushima, C. Curran, and J. V. Quagliano, *J. Am. Chem. Soc.*, **79**, 1575 (1957).

(5) H. L. Schläfer, *Z. Physik. Chem. (Frankfurt)*, **11**, 65 (1957).

However, for both pairs of ligands, the position of the ${}^2E_g \leftarrow {}^4A_{2g}$ spin-forbidden transition is essentially unaffected by chelation, as would be expected.

The visible spectrum of the biuret complex resembles those of the oxalate, malonate,⁵ and malonamide⁶ complexes, both in position of the bands and in their intensities, more than the spectrum of the urea compound. There is an increase in intensity of the broad bands of about 50% on chelation, which is probably a result of the lowered symmetry of the chelate.

In Table III are summarized the values of the ligand field strength, Δ , and the Racah parameters B and C .

TABLE III
LIGAND FIELD PARAMETERS FOR CHROMIUM(III)
COMPLEXES (CM⁻¹)

	Urea	Imidazolidone	Biuret
Δ	16,130	16,130	17,240
B	644	644	613
C	3,640	3,655	3,600
${}^2T_{1g} \leftarrow {}^4A_{2g}$	Calcd 16,100	16,140	15,790
	Exptl 15,050	15,050	15,220
${}^2T_{2g} \leftarrow {}^4A_{2g}$	Calcd 23,300	23,400	23,360
	Exptl	20,490

These were calculated from the maxima of the two spin-allowed bands and of the lowest intercombination band from Jørgensen's⁷ solutions to the d^3 determinants of Tanabe and Sugano.⁸ From these parameters, the positions of the other two intercombination bands can be predicted as is also shown in Table III. The results are reasonably good for the ${}^2T_{1g} \leftarrow {}^4A_{2g}$ transition. However, the position of the ${}^2T_{2g} \leftarrow {}^4A_{2g}$ band is predicted to lie some 3000 cm⁻¹ to the blue side of the band observed at 20,490 cm⁻¹. The spectrum at low temperature (Figure 2) shows this band unambiguously, and there seems little doubt that it has been assigned correctly.

The position of the zero-zero bands of the spin-forbidden transitions cannot be fixed precisely. For the imidazolidone compound, the emission and absorption spectra, taken on the same plate, are shown together in

Figure 3. Although the structure is not completely resolved, the region of the two which overlap one another at about 14,400 \pm 50 cm⁻¹ must be close to the true zero-zero energy of the lowest doublet-quartet transition of the complex in a rigid glass.⁹ There is then, in both absorption and emission, one vibronic band of considerably greater intensity which corresponds to a vibrational frequency of about 50 to 100 cm⁻¹ in both the 2E_g and the ${}^4A_{2g}$ states. Because the bands are so broad, *ca.* 60 cm⁻¹, the positions and spacings cannot be estimated any better.

The situation is more complicated for the tris(biuret)-chromium salt, where (Figure 4) the intense emission band centered at about 14,350 cm⁻¹ is actually double on the original plate and consists, as shown in Table II, of two bands at 14,370 and 14,310 cm⁻¹. Since the former appears also in absorption at 14,360 cm⁻¹, it should represent the zero-zero band for the ${}^2E_g \leftarrow {}^4A_{2g}$ transition. On the basis of this assignment, there appear, from the emission spectrum, the vibrational frequencies 60, 260, and 510 cm⁻¹ of the ${}^4A_{2g}$ ground state, and, from the absorption spectrum, the vibrational frequencies 350 and 440 cm⁻¹ of the 2E_g state appear. The band which appears at about 15,200 cm⁻¹ can be assigned to the ${}^2T_{1g} \leftarrow {}^4A_{2g}$ transition.

A final point about the emission spectra of the two complexes is that no fluorescence, *e.g.*, the transition ${}^4T_{2g} \rightarrow {}^4A_{2g}$, could be detected. The urea complex is therefore still the only chromium(III) complex ion for which both phosphorescence and fluorescence have been observed.¹⁰ Although this result is consistent with the other spectral properties of the biuret complex, it is quite unexpected for the imidazolidone complex in view of its great similarity otherwise to the urea complex.

Acknowledgments.—The authors wish to thank the donors of the Petroleum Research Fund, administered by the American Chemical Society, for support of this research.

(6) K. K. Chatterjee, unpublished results.

(7) K. Jørgensen, *Advan. Chem. Phys.*, **5**, 72 (1963).

(8) Y. Tanabe and S. Sugano, *J. Phys. Soc. Japan*, **9**, 753 (1954).

(9) G. B. Porter and H. L. Schläfer, *Ber. Bunsenges. Physik. Chem.*, **68**, 316 (1964).

(10) G. B. Porter and H. L. Schläfer, *Z. Physik. Chem. (Frankfurt)*, **40**, 280 (1964).