sorptions. The infrared spectrum of this solid is different from those of the solid tris complexes. When the Raman and infrared spectra are compared, it is seen that the stronger infrared absorptions either correspond to weak Raman lines or are absent in the Raman spectra. Conversely, the Raman frequencies are weak or else absent in the infrared. Newman and Powell[10] from an infrared study concluded that this compound consists of Zn atoms bridged by ethylenediamine ligands (each with its two N atoms *trans* to the C–C bond). Our observation of lack of Raman–infrared coincidence for the ligand frequencies confirm their conclusions. The observation of two Zn–Cl stretching vibrational frequencies (one of them active in both infrared and Raman spectra) rules out the formulation $(Zn(en)_2)ZnCl_4$. The Zn–N stretching frequency for this complex may correspond to one of the three infrared absorptions in the 400-cm^{-1} region. Another possibility, which seems to be more likely is that this frequency may be much lower, below the 260-cm^{-1} limit of our spectra. Then, the above three lines would be due to skeletal bending vibrations.

[10] G. Newman and D. B. Powell, *J. Chem. Soc.*, 477 (1961).

CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY,
THE UNIVERSITY OF TEXAS, AUSTIN, TEXAS 78712

Deprotonation of Tris(ethylenediamine)osmium Halides

BY GEORGE W. WATT, JAMES T. SUMMERS, E. M. POTRAFKE, AND E. R. BIRNBAUM

Received November 15, 1965

It has been demonstrated that tris(ethylenediamine)osmium(III) iodide can be deprotonated with amide ion or potassium in liquid ammonia or hydroxyl or ethoxyl ions in ethanol. Study of the infrared spectra of the resulting and related species shows that ν(NH) and δ(NH) are only little influenced by change in the oxidation state of the central metal ion.

Deprotonation of ethylenediamine ligands associated with transitional metal ions has been effected in one instance in aqueous solution,[1] anhydrous ethylenediamine,[2] potassium in liquid ammonia,[3,4] and in numerous cases with amide ion in liquid ammonia,[5] including also the deprotonation of diethylenetriamine. Since Dwyer and Hogarth[2] had demonstrated the deprotonation of ethylenediamine complexes of osmium, it was of interest to study deprotonation reactions employing other bases and to determine the effect of changes in the oxidation state of osmium upon properties of the deprotonated species. The results are reported here.

Experimental Section

Methods.—Reactions in liquid ammonia and procedures for handling the products thereof were the same as described elsewhere.[6] For reactions in ethanol at room temperature, the same equipment was used; ethanol stored over CaH_2 was distilled directly into the reactors cooled with Dry Ice–2-propanol. Air-sensitive products were stored and/or transferred in a drybox containing a He atmosphere maintained oxygen- and water-free by continuous exposure to liquid Na–K alloy.

X-Ray diffraction data were obtained using Cu Kα radiation (Ni filter) at 35 kv and 15 ma and exposure times of 8-20 hr; relative intensities were estimated visually. For the complexes for which data were not already available, *d* spacings corresponding to the six most intense lines are given in Table I.

Infrared spectra for Nujol and high-boiling perfluorokerosene (PFK) mulls were recorded with a Beckman IR-7 spectrophotometer with NaCl and CsI interchanges. Data for the 600-3400 cm^{-1} region are given in Table II and Figure 1 and for the 250–700 cm^{-1} region in Table III and Figure 2.

Magnetic susceptibilities were determined at 25° with a Curie–Cheneveau balance calibrated against $HgCo(SCN)_4$; the data were corrected for diamagnetic contributions.

The pK_a value was determined (with an estimated accuracy of ± 0.03 pK_a unit) with a Beckman Model G pH meter calibrated against commercial pH 4.10 and 7.00 buffer solutions. The pK_a value was determined from a titration midpoint for a titration of a 1 m*M* solution of complex with a 0.01 *N* HNO_3 solution; except for employment of dilute solutions, ionic strength was not otherwise controlled.

Materials.—Unless otherwise indicated, all chemicals were reagent grade and anhydrous.

Ammonium hexabromoosmate(IV), $(NH_4)_2OsBr_6$, was prepared as described by Dwyer and Gibson.[7]

β-Aminoethylamidobis(ethylenediamine)osmium(IV) iodide,[8] $[Os(en{-}H)(en)_2]I_3$; bis(β-aminoethylamido)ethylenediamineosmium(IV) iodide and bromide, $[Os(en{-}H)_2(en)]X_2$; and tris(ethylenediamine)osmium(III) iodide dihydrate were prepared by the methods of Dwyer and Hogarth.[2] *Anal.*[9] Calcd for $[Os(en{-}H)(en)_2]I_3$: Os, 25.4. Found: Os, 25.6. Calcd for $[Os(en{-}H)(en)_2]Br_3$: Os, 31.2. Found: Os, 31.0. Calcd for $[Os(en{-}H)_2(en)]I_2$: Os, 30.6; N, 13.5. Found: Os, 30.5; N, 13.5. Calcd for $[Os(en)_3]I_3{\cdot}2H_2O$: Os, 24.2; N, 10.7. Found: Os, 24.3; N, 10.8. The dihydrate (0.6825 g) was dehydrated by

---

[1] B. P. Block and J. C. Bailar, Jr., *J. Am. Chem. Soc.*, **73**, 4722 (1951).

[2] F. P. Dwyer and J. W. Hogarth, *ibid.*, **75**, 1008 (1953).

[3] G. W. Watt, R. E. McCarley, and J. W. Dawes, *ibid.*, **79**, 5163 (1957).

[4] G. W. Watt, L. E. Sharif, and E. P. Helvenston, *Inorg. Chem.*, **1**, 6 (1962).

[5] G. W. Watt and B. J. McCormick, *ibid.*, **4**, 143 (1965), and references therein.

[6] G. W. Watt, *et al.*, *J. Inorg. Nucl. Chem.*, **9**, 311 (1959); *J. Electrochem. Soc.*, **98**, 1 (1951); **102**, 454 (1955).

[7] F. P. Dwyer and N. A. Gibson, *Nature*, **165**, 1012 (1950).

[8] (en–*x*H) denotes an en ligand from which *x* protons have been removed.

[9] Analyses were performed as described elsewhere [G. W. Watt and J. T. Summers, *J. Am. Chem. Soc.*, **88**, 431 (1966)] except that the micro Dumas method gave erratic results in the analysis of $[Os(en{-}H)_3]$.

TABLE I

X-RAY DIFFRACTION DATA

$[Os(en)_3]I_3 \cdot 2H_2O$		$[Os(en)_3]I_3$		$[Os(en-H)(en)_2]I_2$	
d, A	I/I_0	*d*, A	I/I_0	*d*, A	I/I_0
7.16	0.90	4.29	1.00	6.66	0.50
5.20	1.00	3.63	0.80	5.07	1.00
4.46	0.70	3.46	0.70	4.42	1.00
4.17	0.10	3.26	0.60	3.79	0.30
3.66	0.20	3.13	0.60	3.00	0.20
3.36	0.20	2.33	0.10	2.84	0.20
$[Os(en-H)_2(en)]I$		$[Os(en-H)(en)_2]I_3$		$[Os(en-H)_2(en)]I_2$	
d, A	I/I_0	*d*, A	I/I_0	*d*, A	I/I_0
5.13	1.00	7.13	0.40	6.67	0.70
4.38	0.20	5.22	1.00	5.39	0.20
3.02	0.10	4.41	0.70	5.10	1.00
2.86	0.10	4.14	0.30	4.41	0.90
2.12	0.15	3.95	0.10	3.80	0.40
1.58	0.15	2.93	0.10	3.71	0.40

maintaining it at $<10^{-3}$ mm for 9 days; there was no significant weight loss after 3 days and the total weight loss was 30.1 mg as compared with 31.7 mg calculated for complete conversion to $[Os(en)_3]I_3$. Since the anhydrous iodide is very hygroscopic, it was weighed as the dihydrate, introduced into the reaction vessel, and maintained at $<10^{-3}$ mm for 3 days prior to use in reactions.

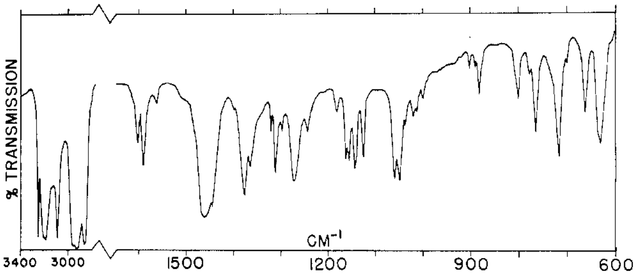

Figure 1.—The infrared spectrum of $[Os(en-H)_2(en)]I_2$ in the 600–3400 cm^{-1} region in a Nujol mull.

During application of the synthesis procedures of Dwyer and Hogarth the following observations of interest were noted: (1) Treatment of $(NH_4)_2OsBr_6$ with anhydrous ethylenediamine at 10° to provide $[Os(en-H)_2(en)]Br_2$ gave low yields and intensely colored filtrates. Dilution of the filtrate with a twofold volume of ethanol precipitated essentially all of the remaining osmium as green crystals that (when wet) darkened rapidly upon exposure to the atmosphere. When dried *in vacuo* over P_4O_{10}, however, the green crystals were stable and gave an infrared spectrum attributable to $[Os(en-H)(en)_2]^{3+}$ and en·HBr. Treatment of this product with NaOH in ethanol (a multiphase reaction with only mild agitation) gave a pink-brown product (identified as $[Os(en-H)_2(en)]Br_2$) while reaction with HI in ethanol gave a mixture of $[Os(en)_3]I_3 \cdot 2H_2O$ and $[Os(en-H)(en)_2]I_3$, as indicated by infrared spectra. This afforded a means to conserve osmium and increase over-all yields by treating this precipitate two or three times alternately with ethanol solutions of NaI and KOH to give $[Os(en-H)_2(en)]I_2$, which is an intermediate in the synthesis of other complexes.[2] (2) In an attempt to prepare $[Os(en-H)(en)_2]I_3$ or $[Os(en)_3]I_4$ by reaction between $[Os(en-H)_2(en)]^{2+}$ and HI, a mixture resulted when the product was isolated soon after addition of HI. Upon standing for at least 2 weeks, how-

TABLE II

INFRARED SPECTRA IN THE 600–3400 CM^{-1} REGION (NUJOL MULLS)

$[Os(en-H)_2(en)]Br_2$	$[Os(en-H)_2(en)]I_2$	$[Os(en-H)(en)_2]I_2$	$[Os(en)_3]I_3 \cdot 2H_2O$	$[Os(en-H)(en)_2]I_3$	$[Os(en)_3]I_3$	$[Os(en-H)_2(en)]I$	$[Os(en-H)_3]$	Tentative Assignments
			3500b,u	3450b				ν (OH)
3255s	3250s	3245				3245b	3225vb	ν (NH)
3210sh(?)	3215			3200				
3190b,u	3180b	3178	3140sh	3150b	3135b	3190b	3140-	ν (NH_2)
3093	3105	3090b	3085		3060b,u	3080b	3120vb	
1620w			1613	1623				δ (OH)
1600s	1603	1603					1605sh	
1590	1592	1591				1595vb	1592b	δ (NH)
		1580sh	1573u	1576	1571			δ (NH_2)
1567w	1565sh	1565w	1554	1548	1556			
				1422				
1324w	1322w	1322w	1331	1331	1332			ω (NH_2)
1316	1312	1312u	1308	1308		1313w		
1305w	1298vw				1304		1305b	γ (CH_2)
1277s	1274	1271	1273u	1275sh,w	1277	1262		
1243w	1244w	1244w	1233w	1253	1231w,u		1242	
			1216	1220u	1216w,b			
1192w	1183w	1182						
1169				1169sh				
1163	1163		1164	1158		1162vw,b	1170sh(?)	ω (NH_2)
	1158	1157u	1158		1152		1158b	γ (NH_2)
1144	1143	1144			1136sh	1145w,b		
1129	1125	1122	1121	1117	1120w			
			1113		1113w			
						1095b		
1065s	1063s	1062						
1054s	1052s	1052	1048s	1052s	1046s	1050(?)	1052	ν (CN)
1020w	1023w	1036		1024				
	1017vw			1019		1018b	1017w	
1002vw	1003(?)	1000w	1005vw	996w				ν (CC)
			991w	975vw	990		975vb	γ (NH_2)
908w	904vw	903w						
897vw	892vw	891w						
				886			885b	
887w	884w	883	872					
				874	870	867w,b	845w(?)	ρ (CH_2)
818	802	803						
				816		802		
784s	777sh(?)							
				788	778			
	766	764	754					
				772		763w	765w	ρ (NH_2)
731		741sh						
	716	717	724					
				724	722		722	ρ (CH_2)
703w	700sh							
						706sh		
662sh	663	663						
643s	632s	633						

TABLE III

INFRARED SPECTRA IN THE 250–700 CM^{-1} REGION (NUJOL MULLS)

$[Os(en)_3]I_3 \cdot 2H_2O$	$[Os(en)_3]I_3$	$[Os(en-H)-(en)_2]I_3$	$[Os(en-H)_2-(en)]I_2$
		662 br	663
			633
		583 w	
560	560	558	572
549	549 sh, u	551	543
		516 sh	
498	498	501 u	
			478
			457
437	435 sh	437 u	
425 sh	428 u		
			377 w
		353 w	364 w
315 u	323 u	319	
283 u	280 u	285 br	

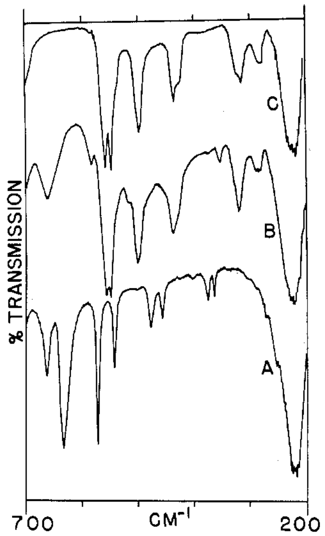

Figure 2.—The infrared spectra of A, $[Os(en\text{–}H)_2(en)]I_2$; B, $[Os(en\text{–}H)(en)_2]I_3$; C, $[Os(en)_3]I_3 \cdot 2H_2O$ in the 200–700 cm^{-1} region in Nujol mulls.

ever, quantitative conversion to $[Os(en)_3]I_3 \cdot 2H_2O$ was effected, as indicated by its X-ray diffraction pattern and infrared spectrum. *Anal.* Calcd for $[Os(en)_3]I_3 \cdot 2H_2O$: Os, 24.2. Found: Os, 24.1.

Synthesis of β-Aminoethylamidobis(ethylenediamine)osmium(III) Iodide.—This complex, $[Os(en\text{–}H)(en)_2]I_2$, was prepared by several means, the most direct of which was treatment of $[Os(en)_3]I_3$ with 1 molar equivalent of KNH_2 in liquid NH_3. Thus, 36.3 mg of K (0.928 mmole) was converted to KNH_2 in 15 ml of liquid NH_3 and added at −33.5° in small portions to a solution and suspension of 0.923 mmole of $[Os(en)_3]I_3$ (from the dehydration of 0.7260 g of $[Os(en)_3]I_3 \cdot 2H_2O$, as described above) in 35 ml of liquid NH_3. From the resulting red solution, pink crystals were obtained by lowering the temperature to −40° by rapid evaporation of the refrigerant NH_3. This product was washed twice with small volumes of NH_3 and dried *in vacuo*. *Anal.* Calcd for $[Os(en\text{–}H)(en)_2]I_2$: Os, 30.5; N, 13.5. Found: Os, 30.6; N, 13.6. The freshly prepared complex was paramagnetic, $\mu_{eff} = 1.58$ BM (under He), but this decreased to *ca.* 1.0 during 12-hr exposure to air and thereafter continued to decrease slowly. Titration of $[Os(en\text{–}H)(en)_2]I_2$ with HNO_3, as described above, gave a midpoint at pH 5.10.

The same deprotonation was effected by treating $[Os(en)_3]I_3 \cdot 2H_2O$ with 3 molar equivalents of K in liquid NH_3 or $[Os(en)_3]I_3$ with 1 molar equivalent of K. In both cases the infrared spectra and X-ray data were identical with those of the product of deprotonation *via* NH_2^-. *Anal.* Found: Os, 30.6.

Similarly, treatment of $[Os(en)_3]I_3$ in ethanol with a sixfold molar excess of KOC_2H_5 or a fourfold molar excess of KOH yielded $[Os(en\text{–}H)(en)_2]I_2$ that gave the same X-ray pattern, infrared spectrum, and magnetic susceptibility as reported above. *Anal.* Found: Os, 30.9; N, 13.5.

Synthesis of Bis(β-aminoethylamido)ethylenediamineosmium(III) Iodide.—The method used to prepare $[Os(en\text{–}H)_2(en)]I$ was the same as for $[Os(en\text{–}H)(en)_2]I_2$ except that slightly more than 2 molar equivalents of KNH_2 was used. The product was a light yellow-brown solid that darkened rapidly on exposure to air. *Anal.* Calcd for $[Os(en\text{–}H)_2(en)]I$: Os, 38.4; N, 17.0. Found: Os, 38.0; N, 17.5. Owing to the solubility of this product in ammonia and its pronounced tendency to peptize, yields were very low and the complex in pure form was not isolated in quantity sufficient for magnetic susceptibility determinations.

Synthesis of Tris(β-aminoethylamido)osmium(III).—The same procedure was used to produce $[Os(en\text{–}H)_3]$ except that 3 molar equivalents of KNH_2 was used; the product was a brown solid. *Anal.* Calcd for $[Os(en\text{–}H)_3]$: Os, 51.8. Found: Os, 52.2. A qualitative test for I^- was negative. Although this complex appeared stable in air, the infrared spectrum of an exposed sample indicated hydration. A sample exposed for 12 hr had an osmium content (Found: Os, 48.2) that suggests both reprotonation and hydration.

Other Attempted Syntheses.—In efforts to produce other deprotonated species with Os in the 3+ or other oxidation states, numerous other reactions were carried out in liquid NH_3; some observations of interest follow.

The reaction between $[Os(en)_3]I_3 \cdot 2H_2O$ and 5 molar equivalents of KNH_2 gave a gray solid that contained 33.6% Os and gave an X-ray pattern that included many of the more intense lines characteristic of $[Os(en\text{–}H)(en)_2]I_2$; this suggests a mixture or an intermediate stage of deprotonation.

Treatment of $[Os(en)_3]I_3$ with 2 molar equivalents of K gave a product that contained 37.5% Os, which is near the range (38.2–38.4% Os) calculated for $[Os(en)_3]I$, $[Os(en\text{–}H)(en)_2]I$, and $[Os(en\text{–}H)_2(en)]I$. This together with an X-ray pattern that included low-intensity lines attributable to $[Os(en\text{–}H)(en)_2]I_2$ also indicates incomplete reaction.

Incomplete reaction also resulted from treatment of $[Os(en\text{–}H)_2(en)]I_2$ with 1 molar equivalent of either K or KNH_2. To the extent that reaction occurred, the products were ammonia-soluble and the residual solid was shown to consist of unreacted starting material by X-ray diffraction data, infrared spectra, and analysis. *Anal.* Calcd for $[Os(en\text{–}H)_2(en)]I_2$: Os, 30.6; N, 13.5. Found: Os, 30.6; N, 13.6.

Treatment of $[Os(en\text{–}H)(en)]I_2$ with 2.5 molar equivalents of KNH_2 afforded a pyrophoric brown solid. *Anal.* Calcd for $[Os(en\text{–}H)_2]I$: C, 14.6; H, 4.3. Found: C, 14.5; H, 4.3. In view of a negative test for I^-, however, the identity of this product remains uncertain. A rather poor infrared spectrum showed very broad bands for ν(NH) and δ(NH) but relatively sharp bands of medium intensity at 2055, 2163, 2227, and 2242 cm^{-1}. After a 17-hr exposure, a faint X-ray diffraction pattern gave *d* spacings (A) of 7.15 (1.0), 6.57 (vw), 4.60 (0.2), 4.08 (vw), 3.33 (vw), and 2.87 (vw). The gram susceptibility was found to be 5.9×10^{-7} cgs unit, which is about that expected for Os(IV).[10]

Discussion

The results reported above show that the first stage in the deprotonation of $[Os(en)_3]I_3$ can be effected by

$$[Os(en)_3]I_3 + \left\{\begin{matrix} K^+ + NH_2^- \\ K^+ + OH^- \\ K^+ + OC_2H_5^- \end{matrix}\right\} \longrightarrow [Os(en\text{–}H)(en)_2]I_2 + \left\{\begin{matrix} KI + NH_3 \\ KI + H_2O \\ KI + C_2H_5OH \end{matrix}\right\} \tag{1}$$

The deprotonation of ethylenediamine ligands by $OC_2H_5^-$ ions has not been observed previously; that by OH^-, in only one case. This is significant in that the use of these ions in solvents such as ethanol will permit deprotonation of halide complexes that in liquid ammonia experience either solvolysis or ligand substitution. The same deprotonation occurs when $[Os(en)_3]I_3$ is treated with potassium in liquid ammonia and, in the absence of an initial liberation of hydrogen, this cannot be attributed to potassium amide formation and subsequent deprotonation by amide ion. Accordingly, it seems likely that, although hydrogen evolution was not measured in the present case, the product can be accounted for by[3]

$$[Os(en)_3]I_3 + K^+ + e^- \longrightarrow [Os(en)_3]I_2 + KI \tag{2}$$

$$[Os(en)_3]I_2 \longrightarrow [Os(en\text{–}H)(en)_2]I_2 + {}^1/_2H_2 \tag{3}$$

---

(10) B. N. Figgis and J. Lewis, "The Magneto-chemistry of Complex Compounds," in "Modern Coordination Chemistry," J. Lewis and R. G. Wilkins, Ed., Interscience Publishers, Inc., New York, N. Y., 1950, Chapter 6.

where (3) is quite slow relative to the rate of (2). An alternative explanation is suggested by the observation that when $[Os(en)_3]I_3$ 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 $[Os(en\text{–}H)(en)_2]I_2$. This, together with the pK_a of 5.1 for $[Os(en)_3]I_3$, suggests that the NH_3 molecule is sufficiently basic to accomplish the deprotonation

$$[Os(en)_3]I_3 + NH_3 \longrightarrow [Os(en\text{–}H)(en)_2]I_2 + NH_4^+ + I^- \quad (4)$$

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 $[Os(en\text{–}H)(en)_2]I_2$ 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 $[Os(en\text{–}H)_2(en)]I_2$ (*vide infra*) except for a sharp band at 675 cm^{-1}. This band can also be brought into the spectrum of $[Os(en\text{–}H)_2(en)]I_2$ 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

$$[Os(en\text{–}H)(en)_2]I_2 + K^+ + NH_2^- \longrightarrow [Os(en\text{–}H)_2(en)]I + KI + NH_3 \quad (5)$$

$$[Os(en\text{–}H)_2(en)]I + K^+ + NH_2^- \longrightarrow [Os(en\text{–}H)_3] + KI + NH_3 \quad (6)$$

The products of these reactions together with the related species prepared by the method of Dwyer and Hogarth[1] 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 $[Os(en)_3]I_3 \cdot 2H_2O$ by rapid crystallization from 99.7% D_2O.[14] The spectrum of $[Os(en\text{–}H)(en)_2]I_2$ is shown in Figure 1 as an example of the spectrum of a deprotonated Os–en complex in the 600–3400 cm^{-1} region even though the bands in the ν(NH) and δ(NH) regions are sharper than those in the spectra of the related complexes.[15] Data in the 250–700 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.

---

[11] The spectral data for $[Os(en\text{–}H)_2(en)]I_2$ in Table II are for a sample that was not ground but simply coated with Nujol and pressed between NaCl plates.

[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 $[Os(en)_3]I_3 \cdot 2H_2O$ is illustrated elsewhere.[8]

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

CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY,
UNIVERSITY OF BRITISH COLUMBIA, VANCOUVER, CANADA

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

BY KUMAR K. CHATTERJEE AND GERALD B. PORTER

Received November 19, 1965

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) perchlorate 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).