Mixed Valence in the Trimeric Oxo- and Nitridoiridium Sulfates

BY DAVID B. BROWN,[1] M. B. ROBIN, J. D. E. McINTYRE, AND W. F. PECK

A number of trimeric oxo- and nitrido-bridged mixed-valence iridium sulfates have been investigated by means of electronic, infrared, and [193]Ir Mössbauer spectra, magnetic susceptibilities, and various electrochemical techniques. The green salt $K_4NIr_3(SO_4)_6 \cdot 3H_2O$ has the trimeric structure which has been postulated in the past and is an Ir(III, IV, IV) class II mixed-valence system, although there appears to be some tendency toward class I behavior. The blue-green oxo-bridged system $K_{10}OIr_3(SO_4)_9 \cdot 3H_2O$ is an Ir(III, III, IV) class II mixed-valence system. This material can be reduced to a yellow Ir(III, III, III) trimer and reversibly oxidized in two one-electron steps to the trimeric Ir(III, IV, IV) and Ir(IV, IV, IV) salts. The chemical, magnetic, and electronic structures of these complexes are discussed.

The aspect of mixed valence[2] adds another dimension to the study of polynuclear transition metal compounds. In a mixed-valence compound, the same element appears in two or more formally different oxidation states. If, however, the ligand fields about the metal ions of formally different valences are identical, then certain of the metal d electrons will be delocalized, yielding nonintegral valences, or equivalently, the integral valences can be considered as oscillating. Materials in which the formally different metal ions are indistinguishable have been termed class IIIa mixed-valence systems. In class IIIa systems the physical properties will be unlike those of any of the integral valence species *formally* present in the ion, just as in a resonating organic system, the real properties of the system are unlike those of any one of the degenerate valence bond resonance structures contributing to it.

On the other hand, if the ligand fields about the metal ions are of a different symmetry and/or strength, then the integral valences will be largely trapped at specific sites. Depending upon the extent of the differences in the ligand fields at the metal ions, such systems are classified as either class I or class II. Unlike class IIIa systems, class I and class II materials will in large part have physical properties (spectra) which are the sum of those of the constituent, integral-valence ions. Though the physical properties of such mixed-valence systems are not in any way unusual, except for their colors, class I and II systems are interesting in that they contain specific valences and specific coordination sites, but one has no general idea of which valences occupy which sites.

Needless to say, if the ions of different valence are not brought within close proximity, there will be no mixed-valence effects and the system will be of little interest. It is easily understood from this that the largest part of the mixed-valence chemistry reported so far involves the solid state and, as such, is as much physics as chemistry. Of greater interest to chemists are the much less ubiquitous mixed-valence polynuclear ions. Such ions, when stable and soluble in the common solvents, offer much more attraction for the chemist than the opaque, microcrystalline powders often encountered in mixed-valence systems. In this paper, we report the results of an investigation of the electronic and molecular structures of a class of stable, water-soluble, mixed-valence polynuclear ions.

Our work is concerned with two iridium complexes which were first reported at the beginning of this century. In a series of papers originating in 1906[3-5] and continuing up to the present day,[6-9] Delépine reported his investigations of the chemistry of a material which he originally believed to be a pure Ir^{III} complex and assigned the formula $K_4H_2NIr_3(SO_4)_6 \cdot 3H_2O$ but which he has since shown to be the mixed-valence salt $K_4Ir_3N(SO_4)_6 \cdot 3H_2O$. Consistent with this formulation, titration of the material with a reducing agent demonstrates the presence of two atoms of Ir^{IV} and one of Ir^{III} per formula.[10] Arguing by analogy to the known structure of the trimeric chromium oxyacetate ion[11] $[Cr_3O(CH_3COO)_6 \cdot 3H_2O]^+$ Jørgensen and Orgel[10,12] proposed the symmetric polynuclear structure
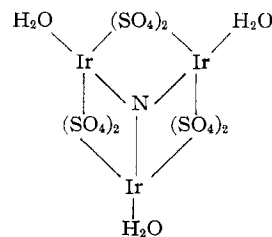
for Delépine's trimer. Though not considered specifically, these authors presumed equivalent ligand fields at the three Ir atoms, thereby placing the material in class IIIa.

Delépine's green trimer is formed by boiling Na_3IrCl_6 and $(NH_4)_2SO_4$ in concentrated H_2SO_4. If the $(NH_4)_2$-SO_4 is omitted, then the deep blue salt of Lecoq de

(1) To whom correspondence should be addressed at the Department of Chemistry, University of Vermont, Burlington, Vt. 05401.

(2) M. B. Robin and P. Day, *Advan. Inorg. Chem. Radiochem.*, **10**, 247 (1967).

(3) M. Delépine, *C. R. Acad. Sci.*, **142**, 631, 1525 (1906); **148**, 557 (1909).

(4) M. Delépine, *Bull. Soc. Chim. Fr.*, **5**, 359, 1084, 1126 (1909).

(5) M. Delépine, *C. R. Acad. Sci.*, **151**, 878 (1910).

(6) M. Delépine, "Nouveau Traite de Chemie Minerale," Vol. XIX, P. Pascal, Ed., Masson et Cie, Paris, 1958, p 516.

(7) M. Delépine, *Ann. Chim. (Paris)*, [13] **4**, 1115 (1959).

(8) M. Delépine and F. Lareze, *ibid.*, [13] **4**, 1131 (1959).

(9) M. Delépine, *C. R. Acad. Sci.*, **251**, 2633 (1960).

(10) C. K. Jørgensen, *Acta Chem. Scand.*, **13**, 196 (1959).

(11) B. N. Figgis and G. B. Robertson, *Nature (London)*, **205**, 694 (1965).

(12) C. K. Jørgensen and L. E. Orgel, *Mol. Phys.*, **4**, 215 (1961).

Boisbaudran is found instead.[13] This material (hereafter referred to as Lecoq's salt) was originally formulated as $Ir_2(SO_4)_3 \cdot 3K_2SO_4$, but subsequent analytical work (below and ref 14 and 15) has shown that Lecoq's salt has the formula $K_{10}Ir_3O(SO_4)_9 \cdot 3H_2O$ and possibly is the oxygen analog of Delépine's salt. If this is the case, then Lecoq's salt *formally* contains two atoms of Ir^{III} and one of Ir^{IV} per trimeric unit.

Experimental Section

Preparation of Compounds. Delépine's Salt.—$(NH_4)_3IrCl_6$ (1 g) was added to 15 ml of concentrated H_2SO_4 and refluxed for 4 hr. The blue-green solution was cooled, diluted with 20 ml of H_2O, filtered, and refrigerated. The solid separating after refrigeration was filtered and washed with methanol. This acidic material was next dissolved in H_2O and passed through an ion-exchange column in the K^+ form. The eluent was reduced in volume and again refrigerated, yielding about 0.5 g of deep green, nonhygroscopic powder. Prior to analysis, the compound was recrystallized once from hot 2% H_2SO_4. *Anal.* Calcd for $K_4NIr_3(SO_4)_6 \cdot 3H_2O$: Ir, 41.86; K, 11.35; S, 13.97; N, 1.02; O, 31.36; H, 0.44. Found: Ir, 41.65; K, 10.66; S, 14.88; N, 0.67; O, 31.34 (by difference); H, 0.80. There are no N–H absorptions in the infrared spectrum of Delépine's salt. Samples grown by slow evaporation of solutions of Delépine's salt in *ca.* 2% H_2SO_4 appeared spongy but under microscopic examination were seen to be crystalline. The material consisted of very small needle-shaped crystals woven together in such a fashion as to resemble steel wool.

Lecoq's Salt.—$Na_2IrCl_6 \cdot 6H_2O$ (2 g) was stirred into 25 ml of concentrated H_2SO_4 and heated nearly to boiling for 2 hr. After cooling, 25 g of K_2SO_4 was added and the mixture was heated in the flame of a Bunsen burner for 1 hr. Following this, the cooled solid mass was extracted with several small portions of H_2O, and the remaining green powder was dissolved in warm H_2O, filtered, and refrigerated. A bright green, microcrystalline material precipitated from the cold solution and was filtered off, washed with cold H_2O, alcohol, and then ether, and air dried. *Anal.* Calcd for $K_{10}OIr_3(SO_4)_9 \cdot 3H_2O$: Ir, 30.31; K, 20.56; S,15.17; O, 33.65; H, 0.32. Found: Ir, 32.67; K, 20.58; S, 14.90; H, 0.39. This green crystalline form of Lecoq's salt differs from the previously reported blue-green Lecoq's salt in a subtle way. The blue-green salt could be precipitated from the filtrate (see above) by the addition of saturated K_2SO_4 solution, and K_2SO_4 precipitation of solutions of the green salt always produced the blue-green salt. Again, the analytical results lead to the formulation $K_{10}OIr_3(SO_4)_9 \cdot 3H_2O$ for the blue-green salt. Found: Ir, 30.38; K, 20.86; S, 14.46; O, 33.80 (by difference); H, 0.50. Lecoq's salt did not appear to be hygroscopic. All measurements and reactions reported in this paper refer to this blue-green salt.

An attempt was made to prepare the selenium analog of Lecoq's salt by a similar procedure utilizing H_2SeO_4. The deep blue material obtained from this reaction could not be adequately purified, but analytical data and infrared spectra indicated that complete reduction of the selenate had occurred, giving a selenite, SeO_3^{2-}, complex.

The once-oxidized Lecoq's (III, IV, IV) complex was prepared by an electrochemical oxidation in 1 N H_2SO_4 followed by precipitation with $Co(NH_3)_6Cl_3$. The resulting product was a mixed $K^+, Co(NH_3)_6^{3+}$ salt, corresponding to the composition $K_6[Co(NH_3)_6]_7[OIr_3(SO_4)_9]_3$. *Anal.* Calcd: Co, 7.19; N, 10.26; H, 2.21; S, 15.10. Found: Co, 7.10; N, 10.07; H, 2.51; S, 14.90.

The vigorous chemical oxidation of Lecoq's salt has been re-

ported to produce a blue material, with all iridium atoms in the +4 oxidation state.[15] We synthesized this material by dissolving 1 g of Lecoq's salt in 20 ml of hot, concentrated H_2SO_4, adding 2 ml of HNO_3, and heating to a rich purple color. The cooled solution was filtered directly into 100 ml of acetone at $-78°$, ether was added, and the gummy blue solid was filtered off. This was immediately redissolved in H_2O, diluted with an equal volume of C_2H_5OH, and again precipitated by the addition of ether. The resulting blue powder was air dried. This unstable material gave a very poor analysis, but the earlier workers[15] assigned it the formula $K_7H_3Ir_3O_2(SO_4)_9 \cdot 2H_2O$.

Physical Measurements.—Analyses were performed by Galbraith Laboratories, Inc., Knoxville, Tenn. Infrared spectra were obtained on a Perkin-Elmer 457 spectrometer using samples pressed into KBr pellets, and electronic spectra were obtained on a Cary 14R spectrometer. X-Ray powder data were collected on film in a 57.3-mm Debye–Scherrer camera using VO_2-filtered Cr $K\alpha$ radiation. No correction was made for film shrinkage, and intensities were estimated visually. Magnetic susceptibilities were measured on a null-coil pendulum magnetometer.[16]

Electrochemistry. (a) Lecoq's Salt.—Lecoq's salt has been studied electrochemically with polarographic, cyclic voltammetric, and rotating-disk electrode (rde) techniques using 1 and 2 mM solutions of the salt in 1 N H_2SO_4. A single polarographic reduction wave with no maximum was observed. The cathodic current rose directly from the anodic mercury dissolution wave, indicating that mercury is oxidizable by the (III, III, IV) iridium salt. Cyclic voltammetric studies were performed using platinum wire and platinum disk electrodes. Two reversible redox couples were observed at +0.3 and +0.9 V *vs.* sce while oxygen evolution precluded observation of a third couple by this technique. Using a platinum rde and rotational speeds, m, ranging from 100 to 10,000 rpm, it was possible to detect one reduction wave ($E_{1/2} = +0.25$ V *vs.* sce) and *two* oxidation waves at +0.92 and +1.42 V *vs.* sce, as illustrated in Figure 1. The second oxidation wave can be observed in this case because of the increased flux and hence greater oxidation rate of the Lecoq anion relative to oxygen evolution.

To determine the number of electrons transferred in each step, a weighed amount of Lecoq's (III, III, IV) salt was quantitatively reduced electrochemically in a coulometric cell having a large mercury pool electrode. The total charge required for the reduction corresponded to the transfer of 1.00 ± 0.01 electron per trimeric unit. From the magnitudes of the limiting currents, I_d, of the oxidation waves (*cf.* Figure 1) it is evident that all steps involve one-electron transfers. From Levich plots of I_d *vs.* $m^{1/2}$, the diffusion coefficient of Lecoq's (III, III, IV) anion in 1 N H_2SO_4 was determined to be $(3.8 \pm 0.1) \times 10^{-6}$ cm^2 sec^{-1}.

(b) Delépine's Salt.—Delépine's salt was also studied electrochemically in 1 N H_2SO_4. A single diffusion-controlled polarographic reduction wave was observed, rising directly from the anodic mercury dissolution wave. Cyclic voltammetric experiments with a platinum wire electrode revealed two reversible redox couples at 0.29 and 1.0 V *vs.* sce. No evidence of a second reduction wave could be detected on Hg, Pt, or Au electrodes.

Results and Discussion

There is a considerable body of evidence which supports the trimeric structure of Delépine's and Lecoq's salts. The careful analytical work of Delépine[6,7] has demonstrated an Ir:N ratio of 3:1; that this is not simply a mixture is demonstrated by the magnetic properties (see below) and by the variety of substitutions which appear to maintain the integrity of the trimeric unit. In a structure such as the one previously

(13) Lecoq de Boisbaudran, *C. R. Acad. Sci.*, **96**, 1336, 1406 (1883).

(14) M. Delépine, "Titres et travaux scientifiques," Imp. Maretheux, 1921, p 10.

(15) S. I. Ginzburg, M. I. Yuz'ko, and L. G. Sal'skaya, *Russ. J. Inorg. Chem.*, **8**, 429 (1963).

(16) R. M. Bozorth, H. J. Williams, and D. E. Walsh, *Phys. Rev.*, **103**, 572 (1956).
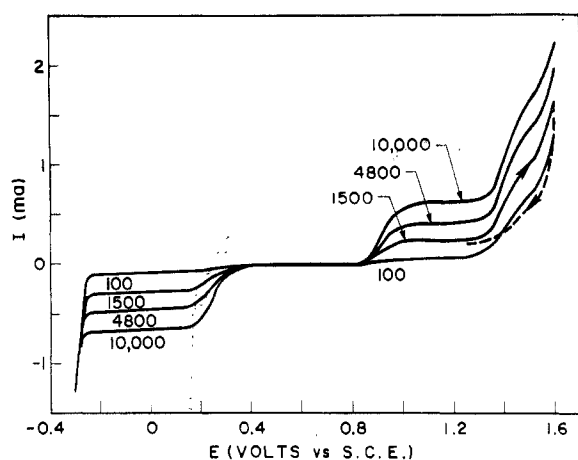
Figure 1.—Steady-state current–voltage curves for the oxidation and reduction of Lecoq's salt; 2 mm in 1 N H_2SO_4, at a Pt rde. Rotational speeds are 100, 1500, 4800, and 10,000 rpm.

proposed, water in the sixth coordination site should be relatively labile, and Delépine has prepared[5,9] products in which three basic ligands have been added to each trimer, e.g., $K_4NIr_3(SO_4)_6(L)_3 \cdot xH_2O$ where L is pyridine, ammonia, or β-picoline. Although a complex containing the μ-nitrido group is unusual, it is not without precedence, for a recent structure determination[17] has confirmed the possibility of nitrido bridging. There are a number of more direct parallels for the oxygen-bridged nature of Lecoq's salt, particularly the trimeric metal oxyacetates mentioned previously, and an oxygen atom bridging three heavier atoms has been confirmed crystallographically in Cr, Fe, and Hg compounds.[11,18,19] The trimeric nature of Lecoq's salt is substantiated by the analytical results and the magnetic and electrochemical investigations described below. Griffith[20] recently examined the low-frequency Raman and infrared spectra of Lecoq's (III, III, IV) salt and concluded that the trimeric structure is correct, although he found evidence for a possible deviation from planarity in the Ir_3O group. The expected frequency for $\nu_s(Ir_3O)$, based on a D_{3h} model, is 125 cm^{-1}, and the observation of this band at 233 cm^{-1} is ascribed to the combined effects of Ir–O π bonding and a possible deviation from planarity. Splitting of the ν_2, ν_3, and ν_4 bands of SO_4^{2-} suggests the presence of bidentate sulfato ligands, in accord with the proposed structure. Delépine's salt also appears to contain bidentate sulfato ligands, as ν_3 (1160 (m), 1137 (s), 1026 cm^{-1} (m)) and ν_4 (680 (w), 610 (m), 598 cm^{-1} (w)) are split.

The difference between the green and blue-green forms of Lecoq's salt is difficult to explain. Analytically and magnetically they appear equivalent, and although their solutions are visually quite distinct, the only distinction between their electronic spectra is in small differences in their relative extinction coefficients and in broadened absorptions for the green salt. Di-

(17) M. Ciechanowicz and A. C. Skapski, *Chem. Commun.*, 574 (1969).
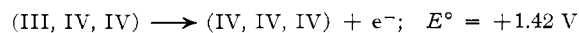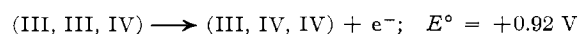(18) K. Anzenhofer and J. J. De Boer, *Recl. Trav. Chim. Pays-Bas*, **88**, 286 (1969).
(19) K. Aurivillius, *Ark. Kemi*, **22**, 517, 537 (1964).
(20) W. P. Griffith, *J. Chem. Soc. A*, 2270 (1969).

lute (*ca.* 1%) H_2SO_4 solutions of the green salt are indistinguishable spectrally from the blue-green salt, and the green color may be regenerated in slightly basic solution, indicating that the green salt is perhaps a deprotonated form of the blue-green salt. However, basic solutions of the blue-green salt are not green, and although the conversion of green to blue-green salt as mentioned above is straightforward, we have been unable to effect the reverse process. That the green and blue-green forms of Lecoq's salt have distinct solid-state structures is clearly reflected in the X-ray powder pattern data given in Table I.

TABLE I
OBSERVED d VALUES AND INTENSITIES FOR THE TWO
DIFFERENT FORMS OF LECOQ'S SALT

Green				Blue-green			
d, Å	I	d, Å	I	d, Å	I	d, Å	I
9.0	100	3.15	20	8.8	90	3.00	100
7.5	40	3.00	20	7.0	30	2.75	40
6.6	70	2.90	20	5.7	10	2.56	30
5.7	30	2.75	10	5.1	10	2.41	10
4.6	10	2.55	10	4.8	10	2.25	20
4.2	10	2.38	20	4.2	10	2.17	20
3.8	20	2.20	30	3.5	20	2.05	10
3.5	20	1.96	20	3.30	10	2.00	10
3.35	20						

Magnetic Properties.—If we presume a triangular structure, for which the orbital degeneracy can be no higher than 2, a simple accounting of the metal atom valences (Ir^{III}, $5d^6$; Ir^{IV}, $5d^5$) shows that Lecoq's (III, III, IV) salt must be a spin doublet, whereas Delépine's (III, IV, IV) salt may be either a singlet or a triplet, depending upon the degeneracy of the uppermost filled MO. In order to check this, the susceptibilities of these materials were measured between room temperature and 1.4°K. Lecoq's salt has a susceptibility closely following a Curie law from 295 to 1.4°K, with a Weiss constant, θ, equal to 0.0. Neglecting both diamagnetic and temperature-independent paramagnetic corrections to the susceptibility, the slope of the $1/\chi_m$ *vs.* T plot gave an effective moment $\mu_{eff} = 1.87$ BM, indicating one unpaired electron per trimeric iridium unit, as expected. Notice that the constancy of the effective moment over the entire temperature range and its value preclude the possibility that Lecoq's salt is, say, hexameric, with two localized spins, but are still consistent with a hexameric unit with two parallel spins in a pair of degenerate MO's (μ_{eff}(calcd) = 2.83 BM; μ_{eff}(obsd) = 2.65 BM).

For Delépine's salt at room temperature, we measure a molar magnetic susceptibility (61.4 $\times$ 10^{-6} cgsu) less than one-twentieth as large as that measured for Lecoq's salt at the same temperature (1447 $\times$ 10^{-6} cgsu), clearly showing that Delépine's salt has no unpaired electrons. The small nonzero positive susceptibility of Delépine's salt results from the imperfect cancellation of the diamagnetic and temperature-independent paramagnetic contributions to the susceptibility. In accord with this explanation, we find that the measured susceptibility is temperature independent. If we apply

this net correction to the data on Lecoq's salt, arguing that it would be appropriate for such similar materials, then μ_{eff} is reduced to 1.81 BM, in even better agreement with that expected for a doublet molecule (1.73 BM).

The magnetic susceptibility of Lecoq's salt shows that it contains one unpaired electron in its highest occupied orbital. This can arise if there is one electron in either a singly or a doubly degenerate MO or if there are three electrons in a doubly degenerate MO. On one-electron oxidation, the former case will give a diamagnetic material, whereas in the latter case, a spin triplet will result.[21] We found that Lecoq's (III, III, IV) salt could be completely oxidized electrochemically in a one-electron step in 1 N H_2SO_4 solution (see electrochemistry section, below) and the oxidized (III, IV, IV) ion could be precipitated by the addition of concentrated $Co(NH_3)_6Cl_3$ solution. The precipitate was filtered, washed with water, and air dried. The spectrum of its solution in concentrated H_2SO_4 was identical with that of the (III, IV, IV) ion generated electrochemically *in situ*. The susceptibility of the oxidized salt was measured only at room temperature and was found to be diamagnetic ($\chi_g = 1.05 \times 10^{-7}$ cgsu). The simplest explanation consistent with these results is that Lecoq's (III, III, IV) salt contains only one electron in its uppermost filled orbital and that both Lecoq's (III, IV, IV) and Delépine's (III, IV, IV) salts are closed-shell molecules. This result is in direct contrast to that found for the trimeric chromium oxyacetate ion mentioned above, for in this species, the spins are quite localized on the metal ions, and the magnetic coupling is of the $J_{12}S_1 \cdot S_2$ type.[22] The difference in the magnetic properties of the iridium and chromium trimers is due no doubt to the combined effects of delocalization through mixed valence and the stronger metal–ligand interactions in the former.

Electrochemistry.—Cyclic voltammetric and rotating-disk electrode studies of Lecoq's salt demonstrate the presence of a reversible one-electron reduction and two reversible one-electron oxidations, consistent with the formulation as an Ir(III, III, IV) mixed-valence complex. The three redox waves are most readily interpreted as corresponding to the processes

$$\text{(III, III, IV)} + e^- \longrightarrow \text{(III, III, III)}; \quad E^\circ = +0.25 \text{ V}$$
$$\text{(III, III, IV)} \longrightarrow \text{(III, IV, IV)} + e^-; \quad E^\circ = +0.92 \text{ V}$$
$$\text{(III, IV, IV)} \longrightarrow \text{(IV, IV, IV)} + e^-; \quad E^\circ = +1.42 \text{ V}$$

Since a pH study was not performed, it cannot be stated to what degree the various trimeric species are protonated.

Although a second reduction wave was not observed for Delépine's salt, the existence of only one oxidation wave is consistent with the formulation as an Ir(III, IV, IV) mixed-valence salt. The redox potentials for Delépine's salt are shifted cathodically from the corresponding potentials for Lecoq's salt. As a result, Delé-

pine's (IV, IV, IV) compound does not spontaneously oxidize the solvent, as does the corresponding Lecoq salt. The behavior of Delépine's salt differs from that of Lecoq's salt in another respect. The limiting currents, peak currents, and coulometric "n" value found in reduction of a 2 mM Delépine salt solution were only 20–30% of the corresponding values observed for Lecoq's salt at the same nominal concentration. The spectrum of an exhaustively reduced solution was indistinguishable from that of the starting solution. The reason for this anomalous behavior is not yet understood.

Mössbauer Spectra.—A preliminary investigation of the 73-keV ^{193}Ir Mössbauer spectra of Delépine's and Lecoq's salts at 4°K is consistent with the assumed formulations. Delépine's salt shows two clearly resolved peaks in an approximately 2:1 ratio, and Lecoq's salt appears as a broad asymmetric band, indicating two types of iridium. The existence of two bands in these spectra definitely categorizes both salts as class II mixed-valence systems, since a class IIIa formulation requires all iridium atoms to be equivalent and hence indistinguishable. A more complete investigation of the ^{193}Ir Mössbauer spectra of all of these materials is in progress.

Optical Spectra.—Investigation of the optical spectra of the electrochemically oxidized and reduced forms of Lecoq's salt in 1 N H_2SO_4 revealed that (III, III, III) is readily air oxidized back to (III, III, IV) and that the fully oxidized (IV, IV, IV) species is unstable with respect to the half-oxidized form (III, IV, IV) in dilute acid. This is further evidenced by the absence of a reduction wave for the (IV, IV, IV) form in the cyclic voltammetric studies; this species spontaneously oxidizes the solvent, water. This observation is in accord with the experience of the earlier workers,[15] who found only monomeric hydrolysis products on attempting to generate (IV, IV, IV) using oxidizing agents in dilute acid. They did find, however, that a new blue material could be formed by oxidation in concentrated H_2SO_4 and claimed that it was the (IV, IV, IV) trimer. Following this lead, we repeated the electrochemical preparations in concentrated H_2SO_4 and observed the spectra shown in Figure 2. That of (III, III, III) formed electrochemically is identical with that reported for the material formed by chemical reduction. Significantly, the spectrum of (IV, IV, IV) reported here is very much different from that of the deep blue (IV, IV, IV) powder prepared chemically. Since our (IV, IV, IV) was stable in concentrated H_2SO_4 and could be reduced electrochemically with quantitative recovery of the (III, IV, IV) spectrum, it seems that the fully oxidized material whose spectrum is shown in Figure 2 is the genuine trimer and that the chemically produced material is either a monomeric Ir^{IV} complex or a polynuclear complex containing fewer or more than three Ir atoms. With regard to the deep blue Ir^{IV} complex, Rose, *et al.*,[23] have recently described the preparation of

---

(21) This is true only if the (III, III, IV) and (III, IV, IV) ions have the same geometry, so that the degeneracies of the orbitals do not change on removing an electron.

(22) J. Wucher and H. M. Gijsman, *Physica*, **20**, 361 (1954).

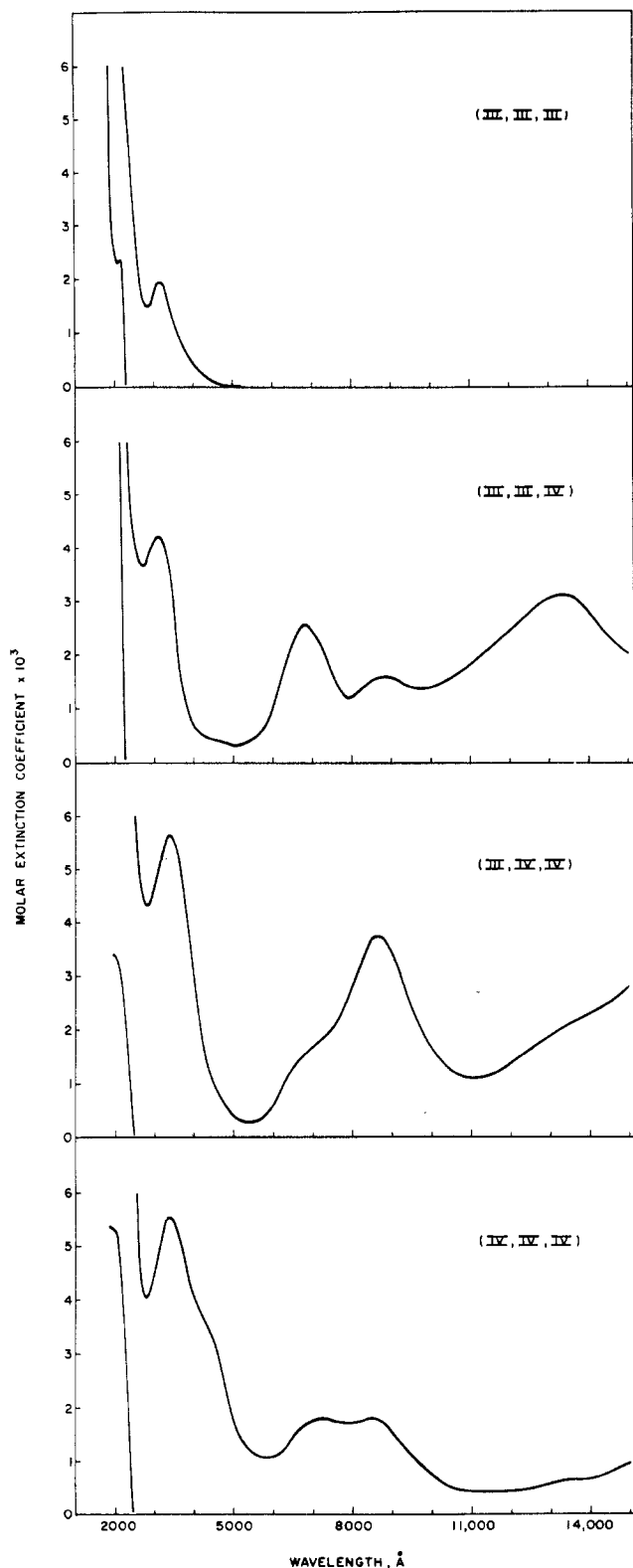(23) D. Rose, R. M. Lever, A. R. Powell, and G. Wilkinson, *J. Chem. Soc. A*, 1690 (1969).

MOLAR EXTINCTION COEFFICIENT x 10³

(III, III, III)

(III, III, IV)

(III, IV, IV)

(IV, IV, IV)

WAVELENGTH, Å

Figure 2.—Optical spectra of Lecoq's salt in various stages of oxidation and reduction. The solvent is concentrated H_2SO_4. The graphs on the left illustrate a scale extension.

an Ir^{IV} iodate in concentrated $HClO_4$ which is deep blue and is thought to be dimeric.

The optical spectrum of a class II mixed-valence polynuclear ion in general consists of the characteristic transitions of the constituent integral valence ions (somewhat shifted usually) and additional transitions

at lower energies which are represented best by an interchange of valence.[2] From Figure 2, we see first that the (III, III, III) trimer shows strong bands only in the uv region between 2000 and 3000 Å. Jørgensen[24] studied the spectrum of the $IrCl_6^{3-}$ ion and finds strong absorption in the 2400–2000-Å region, which he assigned as ligand $\pi \rightarrow$ metal e_g charge transfer. The strong bands in the (III, III, III) spectrum are probably of the same origin, although metal $t_{2g} \rightarrow$ ligand π^* excitations are also imaginable in the sulfates.

Unlike the Ir^{III} ion which has the closed shell 5d-$(t_{2g})^6$ configuration, Ir^{IV} has a hole in the t_{2g} set and hence will show optical absorptions at much lower energies. The two bands observed here in (IV, IV, IV) in the 6000–9000-Å region have their counterparts in the double-peaked structure of the same intensity which Jørgensen reported for the oxidized ion $IrCl_6^{2-}$.[24] These he assigned as charge-transfer transitions from the ligand π orbitals into the t_{2g} hole on the metal. With somewhat altered intensities, these bands are apparent as well in the 6000–10,000-Å region in the mixed-valence salts (III, III, IV) and (III, IV, IV).

By difference then, we are led to assign the strong bands beyond 11,000 Å in the near-infrared region as the mixed-valence transitions in the (III, III, IV) and (III, IV, IV) salts. Since the valences can be considered as trapped in class II compounds, the transition in both cases can be described as involving a valence interchange in the sites A and B: $III_A + IV_B \rightarrow IV_A + III_A$. Such a transition involves the t_{2g} subshells of the iridium atoms and the 2p orbital of the bridging central oxygen atom as well. This latter atom is necessary if the optical electron is to pass between sites A and B with high probability. The possibility that the infrared transitions are really vibrational rather than electronic seems very slim, for the observed intensities are much too high for vibrational bands.

One real possibility for error in the optical spectrum is suggested by the presence of the 3400-Å band in (IV, IV, IV) which is seen to be very prominent in the ions containing Ir(III). It might well be that at the electrode potential used for the final oxidation step, the central oxygen is raised to superoxide ion, O_2^-, leaving the complex as a (III, IV, IV) mixed-valence material. Though this would explain the prominent 36,000-Å absorption as well as the near-infrared tail beyond 14,000 Å, it nonetheless remains to be proved or disproved.

If the oxidized Lecoq (III, IV, IV) and Delépine (III, IV, IV) salts differ only in their central bridging atom, their electronic spectra should be rather similar, except for a possible shift in wavelength. Comparison of the spectrum of Delépine's (III, IV, IV) salt in concentrated H_2SO_4, Figure 3, with that of the corresponding Lecoq salt, Figure 2, shows both similarities and differences. The prominent pair of bands centered at 8000 Å in Lecoq's salt has moved to 6500 Å in Delépine's salt, whereas the string band at 3500 Å in Lecoq's salt seems to have moved to 4600 Å in Delé-

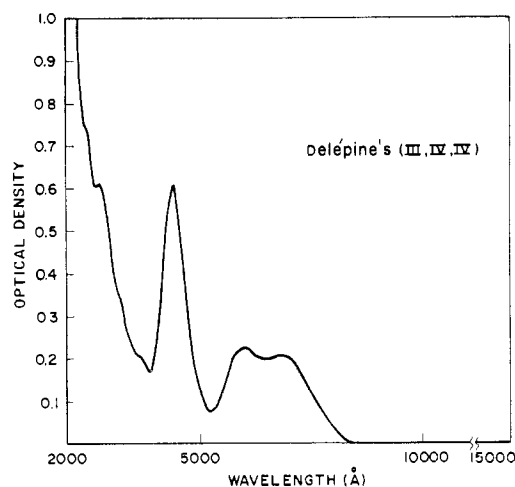(24) C. K. Jørgensen, *Mol. Phys.*, **2**, 309 (1959).

Figure 3.—Optical spectrum of Delépine's (III, IV, IV) salt in concentrated H_2SO_4.

pine's salt. However, unlike Lecoq's salt, the Delépine salt shows no absorption in the 9000–15,000-Å region. Within the framework of the mixed-valence theory,[2] the lack of mixed-valence absorption in Delépine's salt could be taken as the result of a very firm trapping of the valences and a tendency toward class I behavior.

This arises from substantially different ligand fields at the metal atoms of different valence. The preliminary Mössbauer results are also consistent with the idea of Lecoq's (III, III, IV) salt being more class II than Delépine's (III, IV, IV) salt.

Though our experiments directed toward uncovering the structures of these complexes are far less direct than a crystal structure analysis (presently in progress), they do uncover the gross features of the structures. First, all oxidation states of the Lecoq and Delépine salts are trimeric. The ligand fields about the metal atoms of formally different valence are sufficiently different in the mixed-valence ions that the integral valences may be considered as trapped, in the lowest approximation. However, sufficient delocalization of the valences is present to pair all electron spins, except in odd electron species. The close parallel in the properties of the Lecoq and Delépine systems demonstrates that they have very similar structures.

The Heat Capacity of Potassium Perbromate, KBrO₄, between 5 and 350°K[1]

BY FELIX SCHREINER,* DARRELL W. OSBORNE, ALPHONSUS V. POCIUS, AND EVAN H. APPELMAN

The heat capacity of crystalline potassium perbromate has been measured by an adiabatic technique between 5 and 350°K. The standard entropy, enthalpy increment, and Gibbs energy function have been calculated as functions of the temperature. At 298.15°K these functions have the respective values $S° = 170.09 \pm 0.17$ J deg⁻¹ mol⁻¹, $H° − H°_0 = 23,400 \pm 24$ J mol⁻¹, and $−(G° − H°_0)/T = 91.605 \pm 0.092$ J deg⁻¹ mol⁻¹, and $C_P°$ is 120.17 ± 0.12 J deg⁻¹ mol⁻¹. The standard Gibbs energy of formation from the elements at 298.15°K has the value $\Delta G_f° = −174.1 \pm 0.6$ kJ mol⁻¹. In aqueous solution at 298.15°K the standard entropy of the perbromate ion has the value $S° = 199.8 \pm 1.6$ J deg⁻¹ mol⁻¹ on the conventional scale with $S°(H^+, aq) = 0$. The standard entropies of all the halate and perhalate ions are compared, and comments are made on the exceptionally low entropy of the iodate ion, IO_3^-.

Introduction

With the synthesis of perbromates a problem was solved that had been puzzling inorganic chemists for a long time. Although both chlorine and iodine are readily oxidizable to the highest valence state expected for elements of the seventh group, all attempts to produce compounds of heptavalent bromine remained unsuccessful until recently, when perbromate ions were shown to exist by a radioactive tracer technique and the first weighable amount of rubidium perbromate was

obtained by oxidation of bromate ions with xenon difluoride.[2] Subsequent development of the method of oxidizing bromates with elemental fluorine made the large-scale preparation of potassium perbromate feasible.[3] This method was used for the production of the sample used in the present measurements.

The study of the thermodynamic properties of perbromates is of obvious interest, as it furnishes quantitative data relating to the differences between the chemical behavior of heptavalent bromine and that of heptavalent chlorine and iodine. An essential contribution

---

(2) E. H. Appelman, *J. Amer. Chem. Soc.*, **90**, 1900 (1968).
(3) E. H. Appelman, *Inorg. Chem.*, **8**, 223 (1969).