Contribution from the Departments of Chemistry and Physics,
Tulane University, New Orleans, Louisiana 70118

Electrical, Magnetic, and Spectroscopic Properties of $CsNiI_3$

G. L. McPHERSON,*[1a] JOSEPH E. WALL, Jr.,[1a] and ALLEN M. HERMANN[1b]

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Cesium nickel triiodide is isomorphous with $CsNiCl_3$. The $CsNiCl_3$ structure consists of infinite linear arrays of octahedra sharing faces with the nickel ions at the centers and the halide ions at the corners. Electrical resistance measurements of single crystals show that $CsNiI_3$ has a resistivity of 10^7 to 10^8 ohm cm at room temperature with an energy of activation for conduction of approximately 0.7 eV. The conductivity shows very little anisotropy. The electronic spectrum of $CsNiI_3$ shows an intense absorption edge at 1.4 to 1.6 eV, about twice the energy of activation for conductivity. The electrical properties of $CsNiI_3$ are consistent with those of a semiconductor in the intrinsic region. Similar measurements of crystals of NiI_2 indicate that both NiI_2 and $CsNiI_3$ have basically the same electrical properties. The magnetic susceptibility of $CsNiI_3$ deviates noticeably from Curie-Weiss behavior at liquid nitrogen temperature indicating the presence of significant antiferromagnetic coupling. A comparison of the magnetic properties of $CsNiI_3$ to those of $CsNiF_3$, $CsNiCl_3$, and $CsNiBr_3$ suggests that indirect (through ligand) exchange is responsible for the antiferromagnetism.

Introduction

A large number of salts of the formula $M^IM'^{II}X_3$ (where M(I) is a large univalent cation, M′(II) a divalent transition metal ion, and X a halide ion) have been prepared and characterized. Many of these halides adopt either the $CsNiCl_3$ structure or a structure which is closely related to that of $CsNiCl_3$. These hexagonal structures can be described as consisting of infinite parallel chains of octahedra sharing faces where the transition metal ions occupy the centers and the halide ions occupy the corners. The univalent cations hold positions between chains (see Figure 1). The chains run parallel to the crystallographic *c* axis. The spectroscopic and magnetic properties of these salts are currently of interest, since the materials appear to behave as one-dimensional linear antiferromagnets. As a part of a systematic study of these compounds, $CsNiI_3$ was prepared and shown to be isostructural with $CsNiCl_3$.[2] The dark shiny appearance of the iodide salt suggested that the material might possess properties such as electrical conductivity characteristic of metallic or semimetallic substances.

The electrical properties of linear chain systems such as $CsNiI_3$ would be quite interesting if the mechanism for electrical conduction involves the migration of charges along the chains of metal ions. One would then expect single crystals to behave as one-dimensional (parallel to the *c* axis) conductors. The salts, $BaVS_3$ and $BaTaS_3$, have been shown by Wold and coworkers to be isostructural with $CsNiCl_3$.[3,4] (In these compounds the transition metal is in the 4+ oxidation state.) The vanadium salt is a metallic conductor, while the tantalum salt behaves as a semiconductor.[3,4] The conduction in these sulfides is assumed to result from an overlap of the metal d orbitals. Unfortunately, the anisotropy of the conductivity in these materials was not studied, because suitable single crystals could not be obtained.

In light of these considerations a study of the electrical resistance of single crystals of $CsNiI_3$ was undertaken. The electronic spectrum and magnetic susceptibility of $CsNiI_3$ was also studied in order to more fully characterize the material. The spectroscopic and magnetic properties of $CsNiI_3$ can be compared to those of the analogous fluoride, chloride, and bromide salts.

Experimental Section

Preparation of Materials. Equimolar amounts of $NiCO_3$ and CsI were dissolved in concentrated HI solution (47% HI). The solution was filtered and heated to 80–90° under a slowly flowing stream of nitrogen gas. As the solution slowly evaporates $CsNiI_3$ crystallizes as long hexagonal rods. This process takes place over a period of several days. (Note: the evaporation of the HI solution must be carried out at high temperatures or CsI will precipitate out of solution.) The crystals were washed with hot concentrated HI and dried under vacuum at 80°. This method yielded crystals large enough for electrical measurements. The material is very hygroscopic and must be handled in a dry atmosphere. *Anal.* Calcd for $CsNiI_3$: Ni, 10.26; I, 66.52. Found: Ni, 10.2; I, 66.1.

Anhydrous NiI_2 was prepared by dissolving $NiCO_3$ in HI and evaporating the solution at 80 to 90°. The material was then heated to 200° under vacuum and finally purified by vacuum sublimation at 200°. The sublimation was carried out in evacuated Vycor ampoules. Like $CsNiI_3$, NiI_2 is very hygroscopic.

Magnetic Susceptibility Measurements. The magnetic susceptibilities of powdered samples of $CsNiI_3$ were determined by the Gouy method. The apparatus was calibrated with $HgCo(SCN)_4$ used as a reference.[5] Measurements at low temperatures were made using a dewar fitted between the pole faces of a 4-in. magnet. This dewar was successively filled with liquid nitrogen, Dry Ice in acetone, and ice in water to give constant temperatures. A copper–constantan thermocouple was mounted in close proximity to the sample container to measure the sample temperature. The molar susceptibilities were corrected for atomic diamagnetism using the values reported by Mulay.[6] The absolute values of the susceptibilities obtained in this study are probably accurate to only ±5% due to packing errors; however, the internal accuracy should be considerably better.

Spectroscopic Measurements. The mull spectra of $CsNiI_3$ and NiI_2 were studied in the 5,000- to 15,000-cm^{-1} region at room and liquid nitrogen temperature using a Cary 14 spectrophotometer. The mulls were prepared in a drybox using Kel-F grease and were supported between glass plates. A mull of $CaCO_3$ was used as a scattering reference.

Electrical Resistance Measurements. Measurements of the temperature dependence of resistivity were performed under dry nitrogen gas in a Pyrex cylinder equipped with electrical feed-throughs sealed in epoxy. Because of the air sensitivity of the samples, electrodes were attached with Du Pont No. 4817 conductive silver paint in a nitrogen filled drybox. The cylinder was then mounted in a variable temperature bath and placed in an electrostatically shielded enclosure. A copper–constantan thermocouple inside the cylinder near the sample was used to determine the sample temperature, and no hysteresis was noted on cycling the sample up and down in temperature. The resistivity was measured with a two-probe technique utilizing a 90-V battery and a Keithley Model 603 electrometer. Ohmicity of the contacts was verified by linear current-voltage curves

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(1) (a) Department of Chemistry; (b) Department of Physics.

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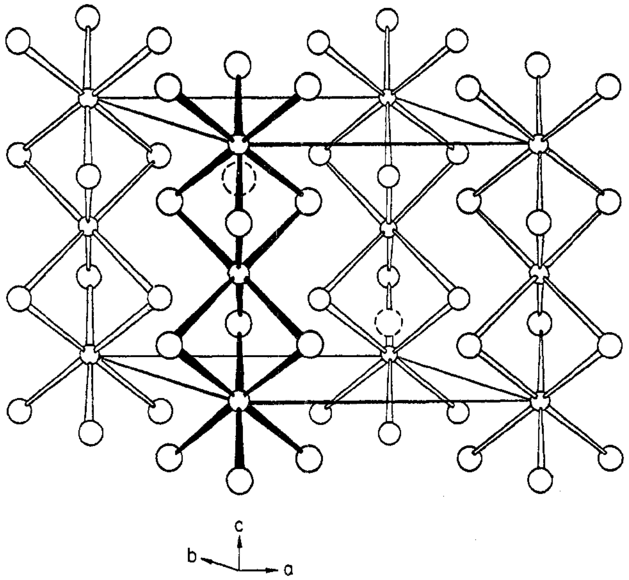

Figure 1. A perspective view of the unit cell contents of a CsNiCl$_3$ type structure. The large open circles represent the halide ions, the small open circles the nickel ions, and the dotted circles the cesium ions.

measured at each temperature. The resistivities were calculated from the resistances using $\rho = R(A/l)$, where R is the resistance, A the cross-sectional area of the sample, and l the length of the sample. The dimensions of the single-crystal samples were determined by examination under a microscope equipped with an optical scale. Because of the small size (~0.5 mm × 0.5 mm × 2.0 mm) and the somewhat irregular shape of the samples, the resistivities are subject to considerable error. The values are expected to be accurate within an order of magnitude.

Results and Discussion

Electrical Resistivity. The electrical conductivity measurements indicate that the resistivity of CsNiI$_3$ at room temperature is between 10^7 and 10^8 ohm cm. This is at the high end of the range of resistivities expected of semiconducting materials. In the temperature range studied, the resistivity can be described by the expression $\rho = \rho_0 e^{E_a/kT}$, where E_a is the energy of activation for the formation of charge carriers, k is the Boltzmann constant, and T is the absolute temperature. Figure 2 shows a plot of log ρ *vs.* $1/T$ for several CsNiI$_3$ crystals. The conduction both parallel and perpendicular to the crystallographic c axis has an energy of activation of approximately 0.7 eV. The resistivities appear to be the same in both directions. (Our data show the perpendicular resistivity to be somewhat higher than the parallel resistivity; however, the difference is within our estimated error limits.)

In order to compare the electrical properties of CsNiI$_3$ to those of a similar material, the resistivity of NiI$_2$ was also studied. Figure 3 shows a plot of log ρ *vs.* $1/T$ for crystals of NiI$_2$. (Only the resistivity perpendicular to the c axis was measured since the crystals grew as thin sheets.) The activation energy of approximately 0.6 eV and the room temperature resistivity of 10^7 to 10^8 ohm cm indicate that the electrical properties of NiI$_2$ are quite similar to those of CsNiI$_3$.

For an intrinsic semiconductor the energy of activation for conduction, E_a, is equal to half the energy separating the valence and conduction bands in the material. Thus, the resistivity can be written as $\rho = \rho_0 e^{E_g/2kT}$, where E_g is the difference in band energies. It is possible to measure E_g from electronic spectra as well as from resistivity studies. Assuming that CsNiI$_3$ and NiI$_2$ are intrinsic semiconductors, one would expect to obtain E_g values of 1.2 to 1.4 eV from the spectra of these materials ($E_g = 2E_a$). The electronic

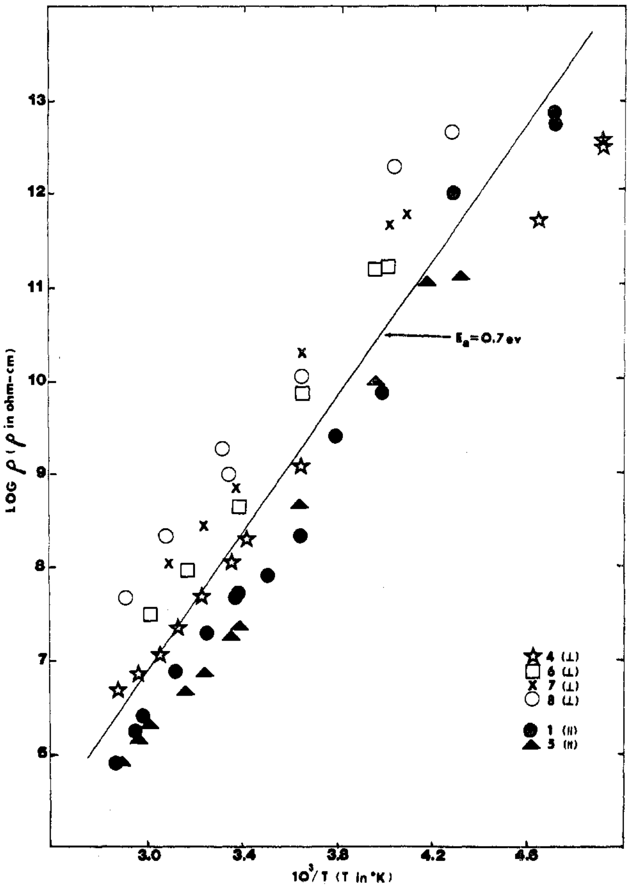

Figure 2. A plot of the log of the resistivity *vs.* the reciprocal of the absolute temperature for several samples of CsNiI$_3$. The resistivities parallel to the c axis are denoted by ∥, while the perpendicular resistivities are designated by ⊥.

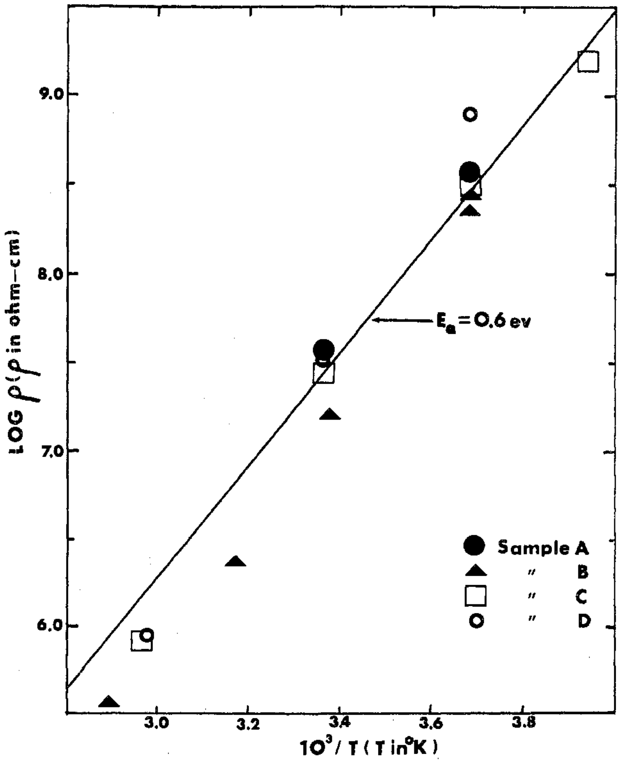

Figure 3. A plot of the log of the resistivity *vs.* the reciprocal of the absolute temperature for several samples of NiI$_2$. All the resistivities are measured perpendicular to the c axis.

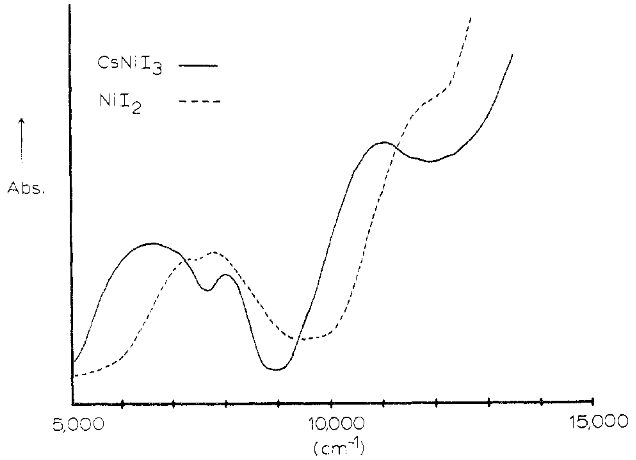

Figure 4. The electronic spectra of $CsNiI_3$ and NiI_2 taken at 77°K. The absorbances are plotted in arbitrary units.

spectra of $CsNiI_3$ and NiI_2 in the near-infrared region contain a number of peaks and shoulders which can be assigned to d-d transitions and a strong absorption edge at 12,000 to 14,000 cm^{-1} (see Figure 4). The materials absorb strongly throughout the visible region. The intense absorption presumably results from the excitation of electrons from the valence band to the conduction band. A measure of E_g can be obtained by determining the minimum energy at which this absorption takes place. The spectra indicate that $CsNiI_3$ and NiI_2 have band gaps of 10,000 to 13,000 cm^{-1} (approximately 1.2-1.6 eV). (The data do not allow extremely accurate determinations, since the d-d transitions complicate the spectra; however, the band gap of NiI_2 appears to be somewhat smaller than that of $CsNiI_3$.) Thus, the spectroscopic and electrical properties of $CsNiI_3$ and NiI_2 are consistent with those of a semiconductor in the intrinsic region.

An attempt was made to study the variation of the resistivity of $CsNiI_3$ with pressure. Unfortunately, the resistances of the samples showed considerable variation with time and reproducible results could not be obtained. It is possible that under pressure $CsNiI_3$ undergoes some sort of structural change which alters its electrical properties. The studies of Longo and coworkers have shown that other salts having the $CsNiCl_3$ structure can undergo pressure-induced structural transformations.[7-9] Wold pointed out that pressure treatment could introduce disorder into the structure of a sample even though a structural change did not occur.[4] Such a disordering could affect the electrical properties of a material.

The observation that the resistivity of $CsNiI_3$ is nearly isotropic is somewhat surprising and perhaps disappointing. Apparently the separation between nickel ions within the anionic chains is too large for significant d orbital overlap. The Ni-Ni distance in $CsNiI_3$ is 3.38 Å which is considerably larger than the V-V separation of 2.80 Å in the metallic conductor, $BaVS_3$. The fact that NiI_2 which adopts the CdI_2 structure has electrical properties similar to those of $CsNiI_3$ suggests that electrical conduction in these materials is not dependent on minor structural details. The CdI_2 structure consists of planar arrays of octahedra sharing edges. These two-dimensional sheets stack parallel to the crystallographic *c* axis.

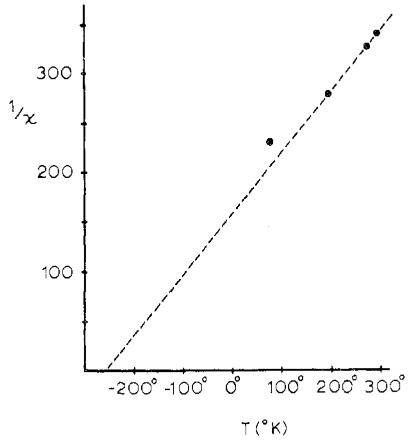

Figure 5. A plot of the reciprocal of the molar susceptibility of $CsNiI_3$ *vs.* the absolute temperature.

Table I. Magnetic and Spectroscopic Data for $CsNiI_3$

Magnetic Susceptibility

Temp, °K	χ_m, $\times 10^6$ esu	$1/\chi_m$
298	2940	340
273	3070	326
196	3610	277
77	4350	230

Curie-Weiss law: $\chi = C/(T - \Theta)$
$\mu_{eff} = 2.84\sqrt{\chi(T - \Theta)}$
For $CsNiI_3$: $\Theta = -250 \pm 25°$
$\mu_{eff} = 3.6$ BM

Ligand Field Spectrum

Transition energy, cm^{-1}	Assignment (octahedral field)
6500	$^3T_{2g} \leftarrow {^3A_{2g}}$
8000	$[^1E_g \leftarrow {^3A_{2g}}]^a$
11000	$^3T_{1g} \leftarrow {^3A_{2g}}$

[a] Tentative.

Magnetic and Spectroscopic Properties. The magnetic susceptibility of $CsNiI_3$ obeys the Curie-Weiss law in the 300 to 196°K region but deviates significantly at liquid nitrogen temperature (see Figure 5). This deviation and the large negative Weiss constant (−250°) are indicative of fairly strong antiferromagnetic coupling. The electronic spectrum of $CsNiI_3$ shows three bands which can be attributed to d-d transitions (see Figure 4). The first band can be readily assigned to the $^3T_{2g} \leftarrow {^3A_{2g}}$ transition whose energy is equal to the crystal field splitting energy, Δ. The spectral assignments and susceptibility data are given in Table I. Although these studies leave little doubt as to the antiferromagnetic nature of $CsNiI_3$, a complete characterization would require single-crystal measurements at temperatures below 77°K.

The cesium nickel trihalides are rather unique since the same crystal structure is maintained throughout the series from fluoride to iodide. A summary of the magnetic and spectroscopic properties of the $CsNiX_3$ salts is given in Table II. The Weiss constants, Θ, indicate that the dominant magnetic interactions in $CsNiCl_3$, $CsNiBr_3$, and $CsNiI_3$ are antiferromagnetic while those in $CsNiF_3$ are ferromagnetic. Assuming that the magnitude of Θ is directly related to the strength of the magnetic interactions, it is clear that the antiferromagnetic coupling increases substantially in the series going from chloride to iodide.

The magnetic properties of the cesium nickel trihalides are undoubtedly determined to a large extent by the structural characteristics of the salts. Within the $[NiX_3]^-$ anionic chains

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Table II. Magnetic and Spectroscopic Properties of the $CsNiX_3$ Salts

Compd	Ni–Ni distance, Å	Θ, deg	μ_{eff}, BM	Δ, cm^{-1}
$CsNiF_3$	2.61[a]	+8[b]	3.6[b]	--
$CsNiCl_3$	2.96[c]	−76,[d,e] −69[f]	3.37,[d] 3.41[f]	6950[g]
$CsNiBr_3$	3.12[h]	−101[d]	3.42[d]	6550[g]
$CsNiI_3$	3.38[i]	−250[j]	3.6[j]	6500[j]

[a] D. Babel, *Z. Anorg. Allg. Chem.*, **369**, 117 (1969). [b] Reference 10. [c] G. N. Tishchenko, *Tr. Inst. Kristallogr. Akad. Nauk SSSR*, **11**, 93 (1955). [d] Reference 12. [e] Reference 14. [f] Reference 13. [g] G. L. McPherson and G. D. Stucky, *J. Chem. Phys.*, **57**, 3780 (1972). [h] G. D. Stucky, S. D'Agostino, and G. McPherson, *J. Amer. Chem. Soc.*, 88, 4828 (1966). [i] Reference 2. [j] This work.

the nickel–nickel separations are rather short (2.6–3.4 Å) and each nickel(II) ion shares three halide ions with the neighboring nickel(II) ions. Thus, both direct (through space) and indirect (through ligand) magnetic interactions are possible. On the other hand, the separations between adjacent nickel(II) ions in different chains are considerably larger (6.2–8.0 Å), and there are no bridging ligands. Clearly, the intrachain interactions should be much stronger than the interchain interactions. This has been shown to be true for $CsNiF_3$[10,11] and $CsNiCl_3$[12–15] by magnetic susceptibility and neutron diffraction studies.

Direct exchange interactions are very dependent on interionic separations while indirect exchange is dependent on the degree of covalency in the metal–ligand–metal linkage. Considering the $CsNiX_3$ series, one would expect the direct effects to decrease going from fluoride to iodide, since the Ni–Ni separation increases from 2.6 to 3.4 Å. In contrast the opposite trend would be expected for indirect exchange, since covalency presumably increases going from fluoride to iodide. On the basis of these considerations, the magnetic data suggest that indirect exchange is responsible for the magnetic properties of $CsNiCl_3$, $CsNiBr_3$, and $CsNiI_3$. This conclusion is quite reasonable for systems containing d^8 ions such as nickel(II), since the unpaired electrons occupy the e_g orbitals which are directed toward the ligands. The fact that $CsNiF_3$ is ferromagnetic is somewhat surprising. It is possible that direct rather than indirect exchange is dominant in this material. A second possibility is that the indirect exchange in $CsNiF_3$ leads to ferromagnetic rather than antiferromagnetic coupling. Indirect exchange is known to be quite sensitive to the metal–ligand–metal angle, and the Ni–F–Ni angle in $CsNiF_3$ is somewhat larger (80°) than the Ni–Cl–Ni angle in $CsNiCl_3$ (75°). The Goodenough–Kanamori rules predict ferromagnetic coupling in systems where the metal–ligand–metal angle is 90°.

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Registry No. $CsNiI_3$, 38496-65-0; NiI_2, 13462-90-3.

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Contribution from Oak Ridge National Laboratory,
Oak Ridge, Tennessee 37830

Comparative Solution Chemistry, Ionic Radius, and Single Ion Hydration Energy of Nobelium[1]

R. J. SILVA,[2] W. J. McDOWELL,[3] O. L. KELLER, Jr.,* and J. R. TARRANT

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The chemistry of nobelium has been examined by comparing its behavior with other elements in solvent extraction and ion-exchange systems, by confirming that its normal valence is 2+ by acid dependence of its solvent extraction behavior, by derivation of its ionic radius using both experimental and theoretical methods, and by calculation of the single ion heat of hydration. In the experimental work about 500–1000 atoms per experiment of cyclotron-produced ^{255}No ($T_{1/2}$ = 223 sec) were used. Its extraction behavior in a tri-*n*-octylamine–HCl system was compared with that of divalent mercury, cadmium, copper, cobalt, and barium and it was found to be most similar to the relatively noncomplexing alkaline earths. Comparison to the alkaline earths in a cation-exchange resin–HCl system indicated it to be most like Ca^{2+} and comparison with these elements in a bis(2-ethylhexyl)phosphoric acid (HDEHP) liquid–liquid extraction system showed nobelium to have an extraction behavior between that of Ca^{2+} and Sr^{2+}. The extraction of nobelium into HDEHP as a function of pH allowed a direct determination of the valence as 2+ in confirmation of previous indications. The ionic radius of No^{2+} was estimated from a linear correlation of ionic radius with distribution coefficient for several divalent ions. A value of 1.0 Å was obtained from ion-exchange data and 1.1 Å from liquid–liquid extraction data with theoretical calculations giving a value of 1.1 Å. The single-ion heat of hydration, obtained from a Born type calculation, was −355 kcal (g-atom)$^{-1}$.

Introduction

The work of Maly, Sikkeland, Silva, and Ghiorso[4] showed nobelium to be most stable in acid aqueous solutions in an oxidation state lower than the 3+ state of its neighbors in the actinide series. Their experiments indicated the behavior of nobelium to be consistent with a 2+ state that could be expected to be stabilized by a $5f^{14}$ electron configuration in the No^{2+} ion. Subsequent work by Silva, Sikkeland, Nurmia, Ghiorso, and Hulet[5] assumed the 2+ state for nobelium in acid aqueous solution and determined a No^{3+}–No^{2+} reduction

(1) Research sponsored by the U. S. Atomic Energy Commission under contract with the Union Carbide Corp.

(2) Presently on leave at the Institut fur Anorganische Chemie und Kernchemie der Universitat Mainz, D-65, Mainz, BRD/Germany.

(3) Chemical Development Section A, ORNL Chemical Technology Division.

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