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Bis(alkylcyclooctatetraenyl)actinide(IV) Compounds[1,2]

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Bis(ethylcyclooctatetraenyl) ($C_8H_7C_2H_5{}^{2-}$ = EtCOT) and bis(*n*-butylcyclooctatetraenyl) ($C_8H_7C_4H_9{}^{2-}$ = BuCOT) compounds of U(IV), Np(IV), and Pu(IV) were synthesized and characterized. X-Ray diffraction patterns showed the three $M(EtCOT)_2$ compounds were isomorphous, and the three $M(BuCOT)_2$ compounds were isomorphous in a different structure. The magnetic susceptibilities of $M(EtCOT)_2$ and $M(BuCOT)_2$ compounds (M = 4+ actinide ion) are almost identical with $M(COT)_2$ compounds and suggest a "sandwich" structure for $M(EtCOT)_2$ and $M(BuCOT)_2$. The Mossbauer spectra of all three Np^{4+} compounds are identical within experimental error. Alkyl substitution on the COT ligand results in a shift to longer wavelengths for strong absorption bands in the visible region. This shift is attributed to an increase in electron density on the COT ligands, and these absorption bands are attributed to molecular transitions, rather than 5f-5f transitions of the M(IV) ions.

Introduction

Bis(cyclooctatetraenyl)uranium(IV) [$U(C_8H_8)_2 = U(COT)_2$] was discovered by Streitwieser and Muller-Westerhoff[3] and has been shown by a single-crystal X-ray study to have a sandwich structure with the U^{4+} ion between the two eight-membered COT rings in D_{8h} symmetry.[4,5] The neptunium(IV) and plutonium(IV) analogs[6] were found to be isomorphous with $U(COT)_2$, and the Mossbauer spectrum of the $Np(COT)_2$ demonstrated an unusual degree of covalency for the Np^{4+} ion in $Np(COT)_2$. The almost identical chemical and physical properties of the actinide(IV)-COT compounds suggest that this covalency is also a common property, and the unusually high molecular symmetry makes them attractive for crystal field investigations.[7,8] Because of the high symmetry, $Pu(COT)_2$ demonstrates diamagnetism; the work reported here extends these studies to actinide compounds with ethyl and *n*-butyl substituents on COT, EtCOT and BuCOT.

Experimental Section

Ethylcyclooctatetraene (EtCOT) and *n*-butylcyclooctatetraene (BuCOT) were prepared by the reaction of the proper alkyllithium compound with COT, following the procedure of Cope and Van Orden.[9] The product was separated from the mixture of COT, cyclooctatriene, and alkylcyclooctatrienes by a combination of extraction with concentrated (20-50%) silver nitrate solution and fractional distillation. The identity of the products was verified by infrared spectra.

The preparation of EtCOT and BuCOT compounds of the actinide(IV) ions followed the same general procedure used for preparation of the actinide(IV)-COT compounds.[1,3] EtCOT was reduced to the dianion in tetrahydrofuran (THF) solution by potassium metal at *ca.* −20° in an inert atmosphere, and the stoichiometric quantity of UCl_4, $NpCl_4$, or $[(C_2H_5)_4N]_2PuCl_6$ was added. The mixture was stirred for *ca.* 16 hr and was allowed gradually to warm to room temperature. The crude product was precipitated by adding an equal volume of deaerated water, excess EtCOT was removed by a 2-ml heptane wash, and a pure product was recovered by extraction with toluene and vacuum evaporation of the solvent.

The preparation of bis(tetramethylcyclooctatetraene)neptunium(IV) [$Np(TMCOT)_2$] and its study by nmr have been described.[8]

The techniques used for preparations, manipulations, and experimental measurements on the air-sensitive COT compounds have been previously described.[6]

Results

Analysis. Uranium(IV) compounds were analyzed only for uranium. *Anal.* Calcd for $U(EtCOT)_2$: U, 47.4. Found: 48.1. Calcd for $U(BuCOT)_2$: U, 42.65. Found: 41.5. The instability of these compounds to air prevented successful determinations of carbon and hydrogen content. Infrared spectra showed that the C=C stretching band at 1640 cm^{-1} for the COT ligands was absent in these compounds, indicating planar COT rings.

X-Ray Diffraction Data. Partial X-ray diffraction data are shown in Table I for actinide(IV)-EtCOT compounds, and in Table II for actinide(IV)-BuCOT compounds. These data suggest that the compounds within each series are approximately isostructural, and the crystal structures of each series are different. Combined with the metal analyses for the uranium(IV) compounds, the composition of Np(IV) and Pu(IV) compounds can be inferred from their isomorphism with U(IV) compounds.

Absorption Spectra. The U(IV)-, Np(IV)-, and Pu(IV)-COT compounds each have several strong absorption maxima in the visible region. The absorption spectra of $U(COT)_2$ and of $U(COT)_2$ mixed with $U(EtCOT)_2$ are shown in Figure 1; the spectra of $Np(COT)_2$ and $Np(TMCOT)_2$ are shown in Figure 2. The maxima are listed in Table III. Substitution of alkyl groups on the COT ring shifts the absorption maxima an average of 100 Å to longer wavelengths between $U(COT)_2$ and $U(EtCOT)_2$ or $U(BuCOT)_2$ and about 50-60 Å between $Np(COT)_2$ and $Np(EtCOT)_2$ or $Np(BuCOT)_2$. The maxima of $Np(TMCOT)_2$ are shifted about 350 Å to longer wavelengths than $Np(COT)_2$. The maxima are shifted about 35 Å between $Pu(COT)_2$ and $Pu(EtCOT)_2$ or $Pu(BuCOT)_2$.

Mossbauer Spectra of Np(IV)-COT Compounds. The Mossbauer spectra of $Np(COT)_2$, $Np(EtCOT)_2$, and $Np(BuCOT)_2$ were found to be identical, within the limits of error of the measurements. The parameters obtained from the spectra are listed in Table IV.

Magnetic Susceptibilities. The low-temperature (3-50°K) magnetic susceptibilities of the paramagnetic U(IV)- and Np(IV)-COT compounds are summarized by the convenient, if empirical, Curie-Weiss constants tabulated in Table V. A

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[1] The information contained in this article was developed during the course of work under Contract AT(07-2)-1 with the U. S. Atomic Energy Commission.

[2] A preliminary account of this work was presented at the 163rd National Meeting of the American Chemical Society, Boston, Mass., April 1972.

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[7] N. Edelstein, G. N. La Mar, F. Mares, and A. Streitwieser, Jr., *Chem. Phys. Lett.*, 8, 399 (1971).

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Table I. X-Ray Diffraction Data for Actinide(IV)-EtCOT Compounds

$U(EtCOT)_2$		$Np(EtCOT)_2$		$Pu(EtCOT)_2$	
d, Å	Intens[a]	*d*, Å	Intens	*d*, Å	Intens
7.82	s	7.78	s		
				7.39	m
6.99	w	6.98	w	6.91	w
6.04	w	5.97	w	5.96	w
5.80	s	5.82	s	5.74	m
5.27	s	5.24	m	5.18	m
4.90	w	4.95	w	4.96	m
4.70	s	4.63	s	4.73	m
3.81	s	3.81	s	3.77	s
3.38	m	3.38	m	3.37	w
3.28	m	3.29	m	3.25	m
2.93	w	2.93	m	2.94	m
2.83	m	2.82	m	2.82	w
2.68	m	2.68	m	2.68	m
2.62	m	2.63	m		
2.58	w	2.58	s	2.59	w
2.51	w	2.51	w		
2.42	s	2.40	m	2.40	m
2.32	w	2.34	m	2.34	w
2.26	w	2.27	w	2.28	w
2.16	w	2.17	w	2.18	w
2.13	m	2.12	m	2.12	w
2.04	s	2.03	s	2.03	s

[a] Intensities estimated visually: s, strong; m, medium; w, weak.

Table II. X-Ray Diffraction Data for Actinide(IV)-BuCOT Compounds

$U(BuCOT)_2$		$Np(BuCOT)_2$		$Pu(BuCOT)_2$	
d, Å	Intens[a]	*d*, Å	Intens	*d*, Å	Intens
10.25	s	10.45	m	10.34	m
7.23	m	7.28	w	7.26	w
6.81	s	6.94	s	6.94	s
6.24	s	6.28	s	6.26	s
5.70	m	5.70	m	5.68	s
5.37	s	5.42	m	5.41	s
5.16	s	5.24	m	5.13	s
4.75	w	4.79	w	4.77	w
4.53	m	4.57	m	4.58	m
3.86	m	3.91	m	3.88	m
3.69	w	3.71	w	3.71	w
3.47	m	3.49	w	3.48	w
3.36	m	3.35	m	3.32	w
3.07	w	3.09	w	3.09	w
2.98	w	2.96	m	2.95	m
2.82	w	2.83	w	2.84	w
2.69	m	2.72	m	2.66	w
2.58	m	2.60	m	2.59	w
2.46	w	2.46	w	2.45	w
2.39	w	2.40	w	2.38	w
2.32	w	2.34	w	2.32	w
2.25	w			2.26	w
2.21	w			2.20	w
2.10	m	2.11	m	2.09	w
2.04	w	2.04	w	2.05	w
2.00	m	2.01	m	2.00	w
1.96	w			1.96	w

[a] Intensities estimated visually: s, strong; m, medium; w, weak.

graph of the reciprocal molar susceptibility of $U(COT)_2$ is shown in Figure 3.

Magnetic measurements on $U(COT)_2$, $U(EtCOT)_2$, and $U(BuCOT)_2$ all showed a transition between two magnetic levels at 9 ± 1°K. The magnetic susceptibility of the lowest level of $U(COT)_2$ is represented by $\mu_{eff} = 3.33$ BM and a Θ of 9.4°K; for the higher level, $\mu_{eff} = 2.31$ BM and Θ is 0.0°K. The magnetic constants for $U(EtCOT)_2$ and $U(BuCOT)_2$ are in reasonable, although not exact, agreement with the $U(COT)_2$ values; the transition temperatures were determined from graphs of χT *vs.* T as 9.71°K for $U(COT)_2$, 9.0°K for $U(EtCOT)_2$, and 10.5°K for $U(BuCOT)_2$.

Table III. Major Absorption Maxima for U(IV)-, Np(IV)-, and Pu(IV)-COT Compounds[a]

$U(COT)_2$	$U(EtCOT)_2$	Δ^b	$U(BuCOT)_2$	Δ^c
6150	6260	110	6230	80
6420	6520	100	6510	90
6580	6675	95	6710	130
6810	6910	100	6820	110

$Np(COT)_2$	$Np(EtCOT)_2$	Δ^c	$Np(BuCOT)_2$	Δ^c	$Np(TMCOT)_2$[d]	Δ^c
5175	5210	35	5230	55	5460	285
5610	5665	55	5675	65	5970	360
5820	5870	50	5890	70	6180	360
5980	6030	50	6050	70	6350	370

$Pu(COT)_2$	$Pu(EtCOT)_2$	Δ^e	$Pu(BuCOT)_2$	Δ^e
4040	4080	40	4070	30
4140	4170	30	4170	30
4480	4525	45	4525	45

[a] All wavelengths in Å. [b] Difference from $U(COT)_2$. [c] Difference from $Np(COT)_2$. [d] TMCOT = tetramethylcyclooctatetraene. [e] Difference from $Pu(COT)_2$.

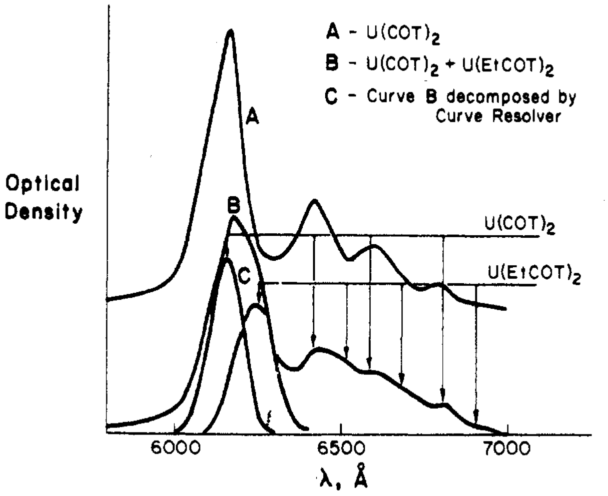

Figure 1. Absorption spectra of $U(COT)_2$ and $U(COT)_2$-$U(EtCOT)_2$ in C_7H_8 solutions.

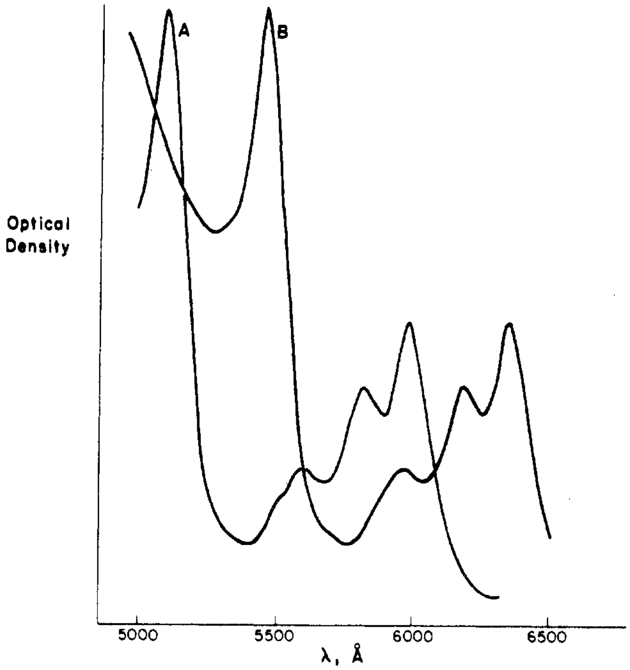

Figure 2. Absorption spectra of $Np(COT)_2$ (A) and $Np(TMCOT)_2$ (B).

Table IV. Mossbauer Parameters of Np-COT Compounds

Compd	Isomer shift,[a] cm/sec	Δ(isomer shift),[b] cm/sec	$g_0 U_N H_{eff}$, cm/sec	Ratio to COT	$^1/_4 eqQ$, cm/sec	Ratio to COT
$Np(COT)_2$	+1.94 ± 0.05		6.12 ± 0.05		−0.46 ± 0.05	
$Np(EtCOT)_2$	+1.90 ± 0.10	$0.00 \left\{\begin{matrix}+0.06\\-0.14\end{matrix}\right.$	6.15 ± 0.10	1.00 ± 0.01	−0.5 ± 0.2	1.0 ± 0.2
$Np(BuCOT)_2$	+1.94 ± 0.05	$0.00 \left\{\begin{matrix}+0.00\\-0.04\end{matrix}\right.$	6.10 ± 0.05	0.9959 ± 0.0001	−0.46 ± 0.05	1.0 ± 0.1

[a] Relative to $NpAl_2$. [b] Difference from $Np(COT)_2$ isomer shift.

Table V. Magnetic Susceptibility Constants for Actinide(IV)-COT Compounds

Compd	Temp range, °K	C,[a] emu °K mol	Θ,[a] °K	μ_{eff}, BM/molecule
$U(COT)_2$	4-10	1.40	9.4	3.33
	10-42	0.69	0.9	2.3
$U(EtCOT)_2$	3-8	1.03	14.9	2.86
	10-27	0.44	0.4	1.9
$U(BuCOT)_2$	3-10	1.01	5.8	2.85
	10-50	0.67	2.6	2.3
$Np(COT)_2$	3-60	0.35	0	1.64
$Np(EtCOT)_2$	3-50	0.41	1.74	1.82
$Np(BuCOT)_2$	3-50	0.37	~0	1.71
$Np(TMCOT)_2$	3-20	0.46	0.62	1.9
$Pu(COT)_2$	Diamagnetic			
$Pu(EtCOT)_2$	Diamagnetic			
$Pu(BuCOT)_2$	Diamagnetic			

[a] Constants from $\chi = C/(T + \Theta)$.

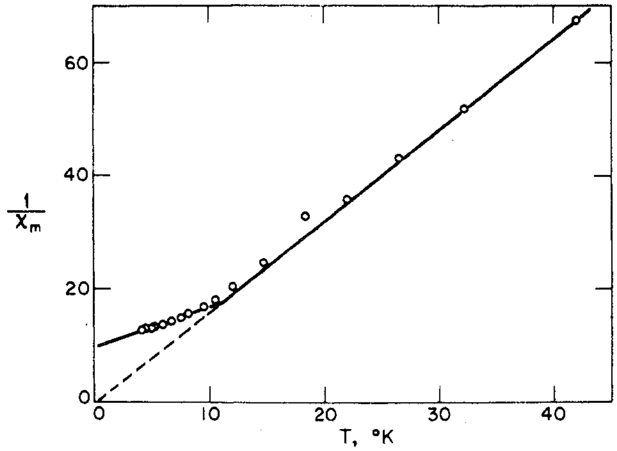

Figure 3. Inverse magnetic susceptibility of $U(COT)_2$.

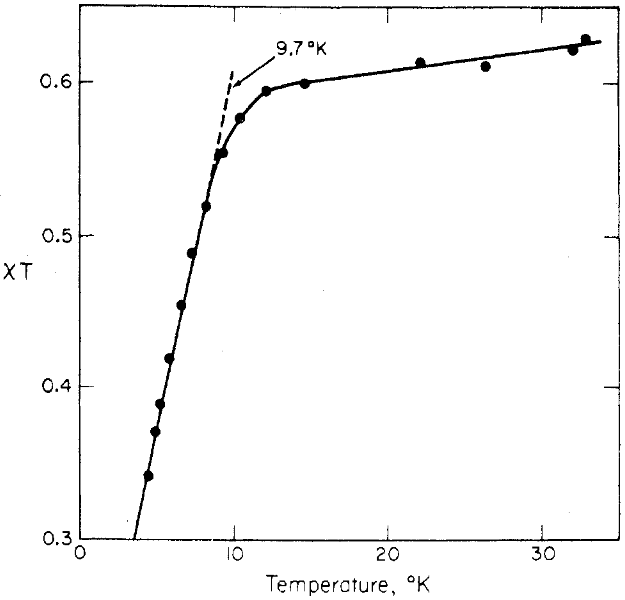

Figure 4. χT vs. T for $U(COT)_2$.

The χT vs. T graph for $U(COT)_2$ is shown in Figure 4. The lowest magnetic level was not recognized as such in earlier[6] measurements on $U(COT)_2$. Larger samples of higher purity and the extension of the operating range down to ~2.5°K both enabled its recognition in this work.

The magnetic susceptibilities of $Np(COT)_2$, $Np(EtCOT)_2$, $Np(BuCOT)_2$, and $Np(TMCOT)_2$ are essentially the same, although the possibility of impurities limits the reliability of the susceptibility constants for $Np(EtCOT)_2$, $Np(BuCOT)_2$, and $Np(TMCOT)_2$. The measurements show a simple paramagnetism, $\mu_{eff} = 1.6$-1.9 BM, and Θ is very small if not zero. The three Pu(IV)-COT compounds are diamagnetic, with an unusual temperature dependence for the diamagnetism.[6]

Discussion

Although different in crystal structure, the actinide(IV)-COT compounds are quite similar in their magnetic susceptibilities; the Mossbauer spectra of Np(IV) compounds are equivalent. Substitution of an alkyl group on the COT ligand increases the solubility of the actinide(IV)-alkylcyclooctatetraene compounds in toluene or benzene compared to actinide(IV)-COT compounds to the potential benefit of nmr studies[7,8] but with the penalty of greater difficulty in purifying the products. The experimental evidence indicates that alkyl substitution on the COT ring does not materially alter the environment of the actinide(IV) ion. Although actinide(IV)-alkylcyclooctatetraene compounds have lower molecular symmetry,[10] the actinide(IV) ion behaves in magnetic susceptibility and Mossbauer measurements as if it were in D_{8h} symmetry, as in $U(COT)_2$.

The shift in the strong absorption bands in the visible region to longer wavelengths indicates that the transitions responsible for these bands are molecular in origin, rather than 5f-5f transitions of the actinide(IV) ion. Comparison of the spectral shifts among $Np(COT)_2$, $Np(EtCOT)_2$, $Np(BuCOT)_2$, and $Np(TMCOT)_2$ indicates that the shifts are roughly the same for ethyl and butyl substitution. The average shift between $Np(COT)_2$ and $Np(BuCOT)_2$ absorption bands is 65 Å; assuming butyl substitution and methyl substitution are equivalent, a shift of 260 Å would be predicted for $Np(TMCOT)_2$. The shift between $Np(COT)_2$ and $Np(TMCOT)_2$ is 360 Å, in fair agreement with the prediction. The difference between predicted and experimental shifts might be attributed to a difference between methyl and butyl substitution of 10-15 Å.

The contribution of electron density to the molecule from alkyl substitution of the COT ligands, on the evidence of Mossbauer spectra, does not cause a detectable change in the electron donation from the ligands to the Np(IV) ion. The absorption bands that are shifted to longer wavelengths are

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(10) K. O. Hodgson, D. Dempf, and K. N. Raymond, *Chem. Commun.*, 1592 (1971).

believed due to molecular transitions rather than to transitions of the Np(IV) ion in a crystalline field.

The improved magnetic susceptibility measurements on $U(COT)_2$, which show a second crystal field level at 9°K, can be rationalized by either of two explanations. The approximate crystal field model originally proposed[6] predicts $J_z = \pm 4$ as the lowest level for the U^{4+} ion in a D_{8h} field, with the next level, $J_z = \pm 3$, several hundred reciprocal centimeters higher. Assuming LS coupling and $\mu_{\text{eff}} = g_j|J_z|\beta$, $\mu_{\text{eff}} = 3.20$ BM for $J_z = \pm 4$ and 2.40 BM for $J_z = \pm 3$. The experimental values are 3.33 BM for the ground level and 2.31 BM for the first excited level, an excellent agreement with this model. However, the energy matrix[6] predicts levels at $-28B_2{}^{\circ}$, $-17B_2{}^{\circ}$, and $8B_2{}^{\circ}$ for $J_z = \pm 4, \pm 3$, and ± 2, respectively. ($B_2{}^{\circ}$ is the second-order crystal field parameter.) For a quantitative agreement, the crystal field level for $J_z = \pm 2$ would be expected at ~20°K. The absence of this level suggests that the predictions of the approximate model cannot be applied in this detail, and the apparent agreement between calculated and experimental magnetic susceptibility values is probably fortuitous.

The failure in detail of the approximate crystal field model requires consideration of an alternate explanation; the most reasonable of which is the probability that the ground state of U^{4+} is split by low-symmetry components in the crystal.[11] This alternative recognizes that, although the molecular symmetry of $U(COT)_2$ is D_{8h}, the $U(COT)_2$ crystal has a monoclinic cell[4,5] and, therefore, has low-symmetry components from the crystal imposed upon the molecule. Splitting of the ground level from these components is reasonable for U^{4+}. Np^{4+}, whose ground state is a Kramers doublet, cannot be split by an electric field and experimentally is not split; Pu^{4+} ($J_z = 0$) cannot be split by any field. The low symmetry of the crystal can show an effect only on U^{4+} in $U(COT)_2$, and splitting of the lowest crystal field level in U^{4+} conforms to this probability. This explanation for the lowest crystal field level of $U(COT)_2$ appears preferable to an explanation based on the approximate crystal field model.

Experimental evidence from absorption spectra, Mossbauer spectra, and nmr studies indicates that the most reasonable theoretical treatment of the actinide(IV)-COT compounds should be on a molecular orbital model. Although an approximate crystal field model[6] can account qualitatively for magnetic susceptibility results, a molecular orbital treatment by Hayes and Edelstein[11] appears successful quantitatively as well. The extension of a molecular orbital treatment to other properties of the actinide(IV)-COT compounds appears promising when additional experimental data are available.

Registry No. $U(COT)_2$, 11079-26-8; $U(EtCOT)_2$, 37274-10-5; $U(BuCOT)_2$, 37274-12-7; $Np(COT)_2$, 37281-22-4; $Np(EtCOT)_2$, 37281-25-7; $Np(BuCOT)_2$, 37281-27-9, $Np(TMCOT)_2$, 12715-86-5; $Pu(COT)_2$, 37281-23-5; $Pu(EtCOT)_2$, 37281-26-8; $Pu(BuCOT)_2$, 37281-28-0.

Acknowledgments. The author is grateful to J. A. Stone for the Mossbauer spectra of the Np(IV)-COT compounds and to N. Edelstein, Lawrence Berkeley Laboratory, for helpful discussions and communication on work in progress. C. A. Harmon and A. Streitwieser, Jr., of the University of California provided a sample of BuCOT for early experiments. R. D. Fischer, University of Erlangen, Nuremberg, proposed the possibility of a lower magnetic state for $U(COT)_2$.

[11] R. G. Hayes and N. Edelstein, *J. Amer. Chem. Soc.*, **94**, 8688 (1972).

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Syntheses and Raman Spectra of Chlorodiiodinium[1] and Bromochloroiodinium Hexachloroantimonates

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The salts chlorodiiodinium hexachloroantimonate, $I_2Cl^+SbCl_6{}^-$, and bromochloroiodinium hexachloroantimonate, $BrICl^+SbCl_6{}^-$, have been prepared by the direct combination of the suitable halogens in the presence of antimony pentachloride. The Raman spectra of these salts have been studied and the mass spectra of their gaseous dissociation products have been observed.

Introduction

Interhalogen compounds can react with either Lewis acids or bases to form cationic or anionic species, respectively. These reactions can be formally described as the self-ionization processes

$$2XY_n \rightleftarrows (XY_{n-1})^+ + (XY_{n+1})^- \quad n = \text{odd, not } 1 \tag{1a}$$

$$2XYZ_m \rightleftarrows (XYZ_{m-1})^+ + (XYZ_{m+1})^- \quad m = \text{even} \tag{1b}$$

where X is the central halogen in each case. The specific conductance of ICl is consistent with the formulation of a polyatomic cation and anion

$$3XY \rightleftarrows X_2Y^+ + XY_2{}^- \quad n = 1 \tag{2}$$

and there is no evidence for monoatomic Cl^+, Br^+, or I^+.[3]

Both I_2Cl^+ and $BrICl^+$ are additions to the family of nonfluorine-containing interhalogen cations of which $ICl_2{}^+$, reported by Vonk and Wiebenga in 1959,[4] had been the only known member. These all can be considered derivable from

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[1] For a preliminary report, see J. Shamir and M. Lustig, *Inorg. Nucl. Chem. Lett.*, 8, 985 (1972).

[2] On sabbatical leave from the Department of Inorganic and Analytical Chemistry, The Hebrew University, Jerusalem, Israel.

[3] R. J. Gillespie and M. J. Morton, *Quart. Rev., Chem. Soc.*, 25, 553 (1971).

[4] C. G. Vonk and E. H. Wiebenga, *Recl. Trav. Chim. Pays-Bas*, 78, 913 (1959).