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CYCLOOCTATETRAENYL NEODYMIUM(III) BROMIDE
AND CYCLOOCTATETRAENYL NEODYMIUM(III) IODIDE

by

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88

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ABSTRACT - Cyclooctatetraenyl neodymium(III) bromide $[\text{Nd}(\text{COT})\text{Br}]$, where $\text{COT} = \text{C}_8\text{H}_8^{-2}$ and $\text{Nd}(\text{COT})\text{I}$ were prepared by the reaction of anhydrous NdBr_3 and NdI_3 with K_2COT in tetrahydrofuran (THF) solution. $\text{Nd}(\text{COT})\text{Br} \cdot 3\text{THF}$ was isolated from the THF solution as a green solid that was extremely reactive to both water and air. The Nd^{3+} ion in $\text{Nd}(\text{COT})\text{Br} \cdot 3\text{THF}$ had two regions of temperature-dependent magnetic susceptibility: $\mu_{\text{eff}} = 2.37\mu_{\text{B}}$ from 2.2 to 17°K, and $\mu_{\text{eff}} = 2.83\mu_{\text{B}}$ from 20 to 48°K. Preliminary studies on the $\text{Nd}(\text{COT})\text{I} \cdot 4\text{THF}$ indicate chemical properties similar to $\text{Nd}(\text{COT})\text{Br} \cdot 3\text{THF}$. Both compounds are analogous to the dimeric $[\text{Ln}(\text{COT})\text{Cl}]_2$ compounds reported by Mares, Hodgson, and Streitwieser [*J. Organometal. Chem.* 28, C24 (1971)].

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INTRODUCTION

Mares, Hodgson, and Streitwieser^(1,2) have prepared and studied lanthanide cyclooctatetraenyl chlorides $[\text{Ln}(\text{COT})\text{Cl}\cdot 2\text{THF}]_2$ ($\text{Ln} = \text{Ce}^{3+}, \text{Pr}^{3+}, \text{Nd}^{3+}, \text{Sm}^{3+}$; $\text{COT} = \text{C}_8\text{H}_8$; $\text{THF} = \text{C}_4\text{H}_8\text{O}$), air- and water-sensitive compounds. The ceric structure involves a chloride bridge between the two Ce^{3+} ions in the dimer⁽³⁾ (Figure 1). Such a structure has the possibility of cooperative magnetic effects through the bridging chlorides, but the possibility might be improved for the bromide or iodide analogues. The synthesis and magnetic susceptibility measurements on $\text{Nd}(\text{COT})\text{I}\cdot x\text{THF}$ and $\text{Nd}(\text{COT})\text{Br}\cdot x\text{THF}$ are presented in this paper.

(1) F. Mares, K. O. Hodgson, and A. Streitwieser, Jr., J. Organometal. Chem. 28, C24(1971).

(2) K. O. Hodgson, Ph.D. thesis, University of California, Berkeley (1972).

(3) K. O. Hodgson and K. N. Raymond, Inorg. Chem. 11, 171 (1972).

EXPERIMENTAL

The purification of solvents, analytical methods, magnetic susceptibility measurements, x-ray diffraction, etc. were performed as previously described.⁽⁴⁾ The compounds were synthesized and purified in a dry argon atmosphere.

(4) D. G. Karraker, J. A. Stone, E. R. Jones, Jr., and N. Edelstein, JACS 92, 4841 (1970).

Cyclooctatetraenyl was vacuum distilled before use. Anhydrous NdBr_3 and NdI_3 were prepared by reacting Nd metal with HgBr_2 or HgI_2 in a sealed, evacuated glass tube at 350°C .

$\text{Nd}(\text{COT})\text{I}\cdot x\text{THF}$ was prepared by adding a stoichiometric quantity of NdI_3 to a -10 to -20°C THF solution of K_2COT . The solution was allowed to warm to room temperature and then stirred for 4 to 20 hours. The reaction mixture was filtered, and the filtrate was vacuum-evaporated to recover the light green product. Calculated for $\text{Nd}(\text{COT})\text{I}\cdot 4\text{THF}$: Nd 21.8, I 19.2. Found: Nd 22.1, I 19.2; Nd/I mole ratio, 1.009.

Attempts to prepare $\text{Nd}(\text{COT})\text{Br}\cdot x\text{THF}$ by the same method produced a mixture of $\text{KNd}(\text{COT})_2\cdot x\text{THF}$ and $\text{Nd}(\text{COT})\text{Br}\cdot x\text{THF}$. This mixture was dissolved in THF and stirred at room temperature with excess NdBr_3 for 3 or 4 days and then filtered; the filtrate was vacuum-evaporated to recover the light green $\text{Nd}(\text{COT})\text{Br}\cdot x\text{THF}$. Calculated for $\text{Nd}(\text{COT})\text{Br}\cdot 3\text{THF}$: Nd 26.3, Br 14.6. Found:

Nd 25.1, Br 13.8; Nd/Br mole ratio, 1.008. The differences from the calculated composition are attributed to occluded solvent in the sample.

The chemical properties of both compounds are similar to those of the $[\text{Ln}(\text{COT})\text{Cl}\cdot 2\text{THF}]_2$ compounds.^(1,2) They are extremely air- and moisture-sensitive, soluble in THF and diglyme [bis(2-methoxyethyl) ether], insoluble in benzene, toluene, and hexane, and decomposed by ethyl alcohol.

RESULTS

X-ray diffraction data for powdered samples of $\text{Nd}(\text{COT})\text{Br}\cdot 3\text{THF}$ and $\text{Nd}(\text{COT})\text{I}\cdot 4\text{THF}$ are shown in Table I, with diffraction data for $\text{KNd}(\text{COT})_2\cdot 2\text{THF}$ included for comparison. Although the data for $\text{Nd}(\text{COT})\text{Br}\cdot 3\text{THF}$ are not particularly good, the differences in the powder patterns indicate three different materials.

The magnetic susceptibility results from 2.2 to 50°K for $\text{Nd}(\text{COT})\text{I}\cdot 3\text{THF}$ and $\text{Nd}(\text{COT})\text{Br}\cdot 4\text{THF}$ are summarized in Table II and shown graphically in Figures 2 and 3. Both compounds have strong temperature-dependent (Curie-Weiss) paramagnetism, and essentially the same in magnetic properties.

DISCUSSION

These preliminary studies of $\text{Nd}(\text{COT})\text{Br}$ and $\text{Nd}(\text{COT})\text{I}$ show no evidence for cooperative magnetic effects above 2.2°K . This can be attributed either to a different molecular structure for the bromide and iodide than the bridged chloride dimer, or to a lack of exchange, even with a favorable geometry. Both are credible; the increase in solvation from the two per Nd^{3+} ion in $[\text{Nd}(\text{COT})\text{Cl}\cdot 2\text{THF}]_2$ to three for $\text{Nd}(\text{COT})\text{Br}\cdot 3\text{THF}$ and four for $\text{Nd}(\text{COT})\text{I}\cdot 4\text{THF}$ suggests differences in structures that could require the increased solvation for shielding of the Nd^{3+} ion. The trivalent lanthanide ions are strongly electronegative ions - very "hard" ions, to use a popular expression - and do not show any marked deviation from normal magnetic behavior until very low temperatures are reached. For example, GdCl_3 has a Curie point at 2.2°K ,⁽⁵⁾ and NdCl_3 has a still lower Curie point, 1.745°K .⁽⁶⁾ The possibility of magnetic exchange depends heavily on the donation of electron density by the electron-rich COT dianion and the bromide or

(5) W. P. Wolf, M. J. M. Leask, B. W. Mangum and A. F. G. Wyatt, J. Phys. Sci. Japan Suppl. B-I, 487 (1961).

(6) J. C. Eisenstein, R. P. Hudson and D. W. Mangum, Phys. Letters 12, 5, (1964).

iodide ion, and could still be insufficient at the lowest temperatures reached in this study, 2.2 to 2.3°K .

The observed magnetic susceptibilities are consistent with the predicted⁽⁷⁾ magnetism for a $J=9/2$ ion in a low symmetric site by either of two explanations.

(7) K. R. Lea, M. J. M. Leask, and W. P. Wolf, J. Phys. Chem. Solids 23, 1381 (1962).

The observed magnetic susceptibility shows two levels, one 10 to 15 cm^{-1} above the ground level. In O_h site symmetry for an Nd^{3+} ion, the lowest crystal field level will be either a Γ_6 (doublet) or a Γ_8 (quartet). In a lower symmetry than O_h , the Γ_8 level would split into Γ_6 or Γ_7 levels. Either a Γ_6 lowest level, with the (split) Γ_8 level 10 to 15 cm^{-1} higher, or the Γ_8 level split by a strong crystal field into two levels 10 to 15 cm^{-1} apart is a possible explanation for the magnetic susceptibility results.

Despite the lack of success in the major purpose of this investigation, $\text{Nd}(\text{COT})\text{Br}\cdot 3\text{THF}$ and $\text{Nd}(\text{COT})\text{I}\cdot 4\text{THF}$ are compounds of considerable interest, both for possible covalent effects in their bonding, and for their potential as intermediates in the synthesis of other neodymium organo-metallic compounds.

TABLE I

PARTIAL X-RAY DIFFRACTION DATA

Nd(COT)Br·3THF			Nd(COT)I·4THF			K ₂ Nd(COT) ₂ ·2THF		
2 θ	d, Å	I	2 θ	d, Å	I	2 θ	d, Å	I
11.49	7.70	M	11.44	7.73	M	10.17	8.69	M
			12.44	7.12	M	10.82	8.18	S
			14.29	6.20	W	12.42	7.13	M
						12.97	6.83	S
15.99	5.54	S				14.42	6.14	W
			17.24	5.14	W	14.97	5.92	M
			18.14	4.89	W	15.62	5.67	W
						16.19	5.48	W
			20.99	4.23	W	16.77	5.29	W
						19.47	4.56	W
22.89	3.89	M	22.84	3.89	W	21.92	4.06	W
			23.39	3.80	W	24.02	3.71	W
			24.54	3.63	W	26.67	3.34	W
25.09	3.55	M	25.19	3.53	W	28.72	3.11	W
						30.62	2.92	W
			27.24	3.27	M	31.42	2.85	W
28.69	3.11	W	30.14	2.96	W	32.89	2.72	W
30.99	2.89	W	31.14	2.87	W	34.22	2.62	W
			31.69	2.82	W	36.92	2.43	W
32.44	2.76	W	32.14	2.78	W	37.77	2.38	W
34.94	2.57	VW	35.69	2.52	W	39.22	2.30	W
36.69	2.45	M	38.74	2.32	W	40.87	2.21	W
			39.54	2.28	W	42.77	2.11	W
40.99	2.20	W	41.94	2.15	W	44.32	2.04	W
						45.57	1.99	W
46.04	1.97	W						

TABLE II

MAGNETIC SUSCEPTIBILITIES FOR Nd(III)-COT COMPOUNDS

Compound	Temp. Range, °K	C^a , emu/°K mole	θ^a , °K	μ_{eff} $\mu_B/\text{molecule}$
Nd(COT)Br·3THF	0-15	0.70	0.84	2.37
	20-90	1.00	7.0	2.83
Nd(COT)I·4THF	0-18	0.70	0.2	2.36
	20-70	0.90	5.1	2.69

a. From the Curie-Weiss expression, $\chi = C/(T+\theta)$

Figure 1. A stereoscopic diagram of the $[\text{Ce}(\text{C}_6\text{H}_8)\text{Cl}\cdot 2\text{C}_4\text{H}_8\text{O}]_2$ complex. Thermal ellipsoids are drawn at the 40% probability contour. Reference 3.

Figure 2. Inverse Magnetic Susceptibility of $\text{Nd}(\text{COT})\text{Br}\cdot 3\text{THF}$

Figure 3. Inverse Magnetic Susceptibility of $Nd(COT)_{1.4}THF$