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BIS(CYCLOOCTATETRAENYL) NP(III) AND PU(III) COMPOUNDS

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BIS(CYCLOOCTATETRAENYL) Np(III) AND Pu(III) COMPOUNDS^{1,2}

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ABSTRACT

Potassium bis(cyclooctatetraenyl) neptunium(III) [KNp(COT)₂, COT = C₈H₈⁻²] and KPu(COT)₂ were prepared as bis-tetrahydrofuran (THF) solvates by reacting the trivalent actinide bromides or iodides with K₂COT in THF solution. X-ray powder patterns indicate that these compounds are isostructural, and the similarity of the powder patterns of KPu(COT)₂·(CH₃OCH₂)₂O with the Ce³⁺ analogue suggests that the Pu³⁺ ion is in a D_{8h} ("sandwich") site in the molecule. The Mössbauer spectrum of the Np(III) compound has an isomer shift (δ) of + 3.92 cm/sec which confirms a +3 valence with only slight covalency, and a quadrupole splitting constant (eqQ/4) of 0.72 cm/sec with zero asymmetry. Magnetic susceptibility measurements on both compounds are reported and discussed in terms of crystal field models.

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(2) This paper was prepared in connection with work under Contract No. AT(07-2)-1 with the U. S. Atomic Energy Commission.

INTRODUCTION

Mares, Hodgson, and Streitwieser have prepared and studied two series of compounds between the cyclooctatetraenyl dianion and trivalent lanthanide ions, $\text{KLn}(\text{COT})_2^3$ and $[\text{Ln}(\text{COT})\text{Cl}\cdot 2\text{THF}]^4$ ($\text{Ln}=\text{La}^{3+}$, Ce^{3+} , etc., $\text{COT}^{2-} = \text{C}_8\text{H}_8^{2-}$, the cyclooctatetraenyl dianion). The structure determination by single-crystal X-ray⁵ of the mono-"diglyme" $[\text{CH}_3\text{OCH}_2]_2\text{O}$ solvate of $\text{KCe}(\text{COT})_2$ showed that the Ce^{3+} ion is at a site of D_{8h} symmetry between the two planar COT rings, like that of U^{4+} in $\text{U}(\text{COT})_2$.^{6,7} This paper reports synthesis and study of the analogous compounds $\text{KNp}(\text{COT})_2$ and $\text{KPu}(\text{COT})_2$.

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- (3) F. Mares, K. Hodgson, and A. Streitwieser, *J. Organometal. Chem.*, **24**, C68 (1970).
- (4) F. Mares, K. O. Hodgson, and A. Streitwieser, *J. Organometal. Chem.*, **28**, C24 (1971).
- (5) K. O. Hodgson and K. N. Raymond, *Inorg. Chem.*, **11**, 3030 (1972).
- (6) A. Zalkin and K. N. Raymond, *J. Amer. Chem. Soc.*, **91**, 5667 (1969).
- (7) A. Avdeff, K. N. Raymond, K. O. Hodgson and A. Zalkin, *Inorg. Chem.*, **11**, (1972).

EXPERIMENTAL

The methods used to purify solvents, analyze compounds, measure magnetic susceptibility, and obtain Mössbauer spectra have been previously reported.⁸ All syntheses, transfer of compounds, and measurements of their properties were performed in a dry argon atmosphere.

Actinide(III) chlorides, bromides, and iodides were prepared by standard methods;⁹ NpCl_3 was prepared by reducing NpCl_4 with powdered zinc at 550°C ; PuCl_3 was prepared by reacting CCl_4 vapor with PuO_2 at 600°C . PuBr_3 was prepared by reacting plutonium metal with HgBr_2 at 350°C ; PuI_3 was prepared by reacting plutonium metal with HgI_2 at 350°C . NpBr_3 and NpI_3 were prepared by reacting 35 wt % Np - 65 wt % Al alloy with the proper mercuric halide.

Preparation Of $\text{KPu}(\text{COT})_2 \cdot 2\text{THF}$ And $\text{KNp}(\text{COT})_2 \cdot 2\text{THF}$. $\text{KPu}(\text{COT})_2 \cdot 2\text{THF}$ was prepared by adding a stoichiometric quantity of either PuBr_3 or PuI_3 to a -10 to -20°C THF solution of K_2COT . The solution was allowed to warm to room temperature and was stirred for at least an hour. The reaction mixture was filtered to remove precipitated

(8) D. G. Karraker, J. A. Stone, E. R. Jones, Jr., and N. Edelstein, *J. Amer. Chem. Soc.*, **92**, 4841 (1970).

(9) D. Brown, *Halides of the Lanthanides and Actinides*, John Wiley, New York (1968).

potassium halide, and the filtrate was vacuum-evaporated to recover turquoise-green $\text{KPu}(\text{COT})_2 \cdot 2\text{THF}$. (Calculated plutonium is 37.88%; determined plutonium was 37.9, 36.8, and 39.1). A test for halides was negative. $\text{KPu}(\text{COT})_2 \cdot 2\text{THF}$ was dissolved in diglyme, and the solution evaporated by vacuum to produce $\text{KPu}(\text{COT})_2 \cdot \text{diglyme}$.

By the same procedure, burgundy-colored $\text{KNp}(\text{COT})_2 \cdot 2\text{THF}$ was prepared from NpBr_3 and K_2COT solution. (Calculated neptunium was 37.7%; determined neptunium was 40.4%). A test for bromide was negative. The X-ray powder diffraction pattern was identical with that of $\text{Pu}(\text{COT})_2 \cdot 2\text{THF}$. The Mössbauer spectrum showed only Np^{3+} in the compound.

Properties Of $\text{KM}(\text{COT})_2 \cdot 2\text{THF}$. These compounds are extremely air- and water-sensitive, like the corresponding $\text{KLn}(\text{COT})_2 \cdot n\text{THF}$ compounds.^{3,4} Traces of oxidizing agents rapidly oxidize solutions to $\text{Pu}(\text{COT})_2$ or $\text{Np}(\text{COT})_2$. $\text{KM}(\text{COT})_2$ compounds were quite soluble in THF, but almost insoluble in benzene or toluene. In some preparations, the $\text{M}(\text{COT})_2$ impurity was separated by extraction with toluene from the solid $\text{KM}(\text{COT})_2 \cdot 2\text{THF}$. Attempts to measure the absorption spectra in THF solution were unsuccessful because the strong absorption by $\text{Np}(\text{COT})_2$ or $\text{Pu}(\text{COT})_2$ impurities obscured the spectra of the trivalent actinide compounds.

Attempts to prepare $\text{KU}(\text{COT})_2 \cdot n\text{THF}$ by the reaction of UBr_3 or UI_3 with K_2COT solution yielded only $\text{U}(\text{COT})_2$. Attempts to reduce $\text{U}(\text{COT})_2$ with potassium, sodium amalgam, or potassium naphthenide either yielded a pyrophoric powder, assumed to be uranium, or no

reaction. Attempts to produce $\text{KPu}(\text{COT})_2$ or $\text{KNp}(\text{COT})_2$ by the reaction of K_2COT with PuCl_3 or NpCl_3 were unsuccessful, possibly because of a very low solubility for the actinide(III) chlorides in THF.

RESULTS

X-Ray Diffraction Data. Partial X-ray diffraction data for $\text{KPu}(\text{COT})_2 \cdot 2\text{THF}$ and $\text{KNp}(\text{COT})_2 \cdot 2\text{THF}$ (Table I) indicate that the two compounds are isostructural. The X-ray diffraction pattern of $\text{KPu}(\text{COT})_2 \cdot \text{diglyme}$, compared in the calculated diffraction pattern of $\text{KCe}(\text{COT})_2 \cdot \text{diglyme}$ in Table II, shows a strong similarity, indicating that the diglyme solvates probably have the same structures for the $\text{KM}(\text{COT})_2 \cdot \text{diglyme}$ compounds.

Mössbauer Spectrum Of $\text{KNp}(\text{COT})_2 \cdot 2\text{THF}$ (Figure 1) is split by an electric quadrupole interaction and shows an isomer shift of +3.92 cm/sec, which establishes the tripositive valence of the neptunium ion in this compound.¹⁰ The quadrupole coupling constant, $1/4 \text{ eqQ}$, equals 0.75 cm/sec with an asymmetry parameter of zero within the resolution of the measurement.

Magnetic Susceptibilities. The magnetic susceptibilities of $\text{KPu}(\text{COT})_2 \cdot 2\text{THF}$ and $\text{KNp}(\text{COT})_2 \cdot 2\text{THF}$ were measured from 2.2 to 80°K, and the data below 50°K are shown in Figures 2 and 3. The Pu^{3+} ion in $\text{KPu}(\text{COT})_2 \cdot 2\text{THF}$ showed a magnetic susceptibility of $\mu_{\text{eff}} =$

(10) D. G. Karraker and J. A. Stone, *Inorg. Chem.*, 11, 1742 (1972).

1.25 μ , $\theta = 3.7^\circ$. The result would be relatively unaffected by an impurity of diamagnetic Pu(COT)₂. The magnetic susceptibility of KNp(COT)₂·2THF has a region of temperature-independent paramagnetism (TIP) from 2.2 to 5.5°K, where $\chi_m = 1.10 \times 10^{-2}$ emu/mole, and two regions of temperature-dependent paramagnetism from 5.5 to 19°K, $\mu_{\text{eff}} = 1.04\mu_B$, $\theta = 6.4^\circ$ and from 19 to 80°K, $\mu_{\text{eff}} = 1.39\mu_B$, $\theta = 26^\circ$. The magnetic susceptibility of KNp(COT)₂·2THF could be severely affected by an impurity of the strongly paramagnetic Np(COT)₂, but this result is considered reliable since Np⁴⁺ (J=9/2) cannot show TIP behavior. A Mössbauer spectrum of the KNp(COT)₂·2THF also showed that Np⁴⁺ was below the detection limit of 5%.

DISCUSSION

Although X-ray powder diffraction patterns do not definitely establish identical structures for actinide(III) and lanthanide(III) KM(COT)₂·2THF compounds, the probability of the trivalent actinide ion having "sandwich" site in KM(COT)₂·2THF is very high. Because the asymmetry parameter is zero for the quadrupole-split Mössbauer spectrum of KNp(COT)₂·2THF, the Np³⁺ ion must be at a site with an n-fold axis, where n is greater than three. When possible ways to arrange the planar COT rings around the Np³⁺ ion are considered, a "sandwich" structure with a D_{8h} or D_{8d} site for the Np³⁺ ion appears the most probable. The differences in X-ray powder patterns might be explained by differences in self-absorption between lanthanide and actinide ions.

The isomer shift of +3.92 cm/sec for Np^{3+} in $\text{KNp}(\text{COT})_2 \cdot 2\text{THF}$ is the largest positive shift yet observed for a $\text{Np}(\text{III})$ ion and is slightly more positive than NpCl_3 ($\delta = 3.54$ cm/sec) or $\text{Np}(\text{C}_5\text{H}_5)_3 \cdot 3\text{THF}$ ($\delta = 3.64$ cm/sec). This isomer shift suggests some degree of covalency of Np^{3+} in $\text{KNp}(\text{COT})_2 \cdot 2\text{THF}$, probably from the contribution of π electron density from the COT^{2-} ligands. However, the covalent contribution is minor in comparison with $\text{Np}(\text{COT})_2$, whose isomer shift is +1.94 cm/sec compared with -0.34 cm/sec for NpCl_4 (Table III). The small covalency of Np^{3+} in actinide(III)-COT compounds, compared with the much large covalent contributions to Np^{4+} in $\text{Np}(\text{COT})_2$, conforms to the pattern established in NpCp_4 and $\text{NpCp}_3 \cdot 3\text{THF}^{10}$ and again indicates that covalency in actinide organometallic compounds depends principally on the valence of the actinide ion.

A possible explanation for the lack of covalency for trivalent actinide COT and Cp compounds, compared to the quadrivalent actinide compounds with the same ligands, probably lies in the difference in size between the +3 and +4 actinide ions. In the large +3 ions, the 5f orbitals are sufficiently shielded that interaction with ligand orbitals is hindered. For the smaller +4 ions the shielding of the 5f orbitals is less, and metal-orbital—ligand-orbital interactions are possible. Extending this argument, +5 and +6 actinides should show a still greater tendency toward covalency. Unfortunately, the synthesis of +5 or +6 compounds with strongly

reducing organic ligands appears extremely improbable.

The small covalent contribution of the actinide(III) ions and their probable high site symmetry in $\text{Knp}(\text{COT})_2 \cdot 2\text{THF}$ and $\text{KPu}(\text{COT})_2 \cdot 2\text{THF}$ presents the possibility that the crystal field model originally proposed⁸ for the actinide(IV)-COT compounds could be applied to the actinide(III)-COT compounds to predict their magnetic properties. In this model, the Np^{3+} ion ($J = 4$) in $\text{KNp}(\text{COT})_2 \cdot 2\text{THF}$ would have $J_z = 0$ in a magnetic field and thus would be diamagnetic, analogous to Pu^{4+} in $\text{Pu}(\text{COT})_2$. The experimental magnetic susceptibility shows a nonmagnetic ground state, and two higher magnetically degenerate levels at ~ 5 and $\sim 15 \text{ cm}^{-1}$. In general, this conforms to the predicted ordering of the levels of $J_z = 0$ as the lowest level, and $J_z = \pm 1$ and $J_z = \pm 2$ as the next levels. Further, the magnetic susceptibility is greater for the $J_z = \pm 2$ level than for $J_z = \pm 1$. The TIP observed for the lowest level can be accounted for by either weak second-order crystal fields or the magnetic field mixing the $J_z = 0$ wave functions with $J_z = \pm 1$ wave functions. The MO model of Hayes and Edelstein¹¹ predicts $J_z = 0$, $J_z = \pm 1$, and $J_z = \pm 3$ for the three lowest levels of the isoelectronic Pu^{4+} ion in $\text{Pu}(\text{COT})_2$, with the magnetic susceptibilities of 0, $1.47\mu_B$, and $1.35\mu_B$, respectively. Adjustments of this calculation for Np^{3+} might lead to a reasonable fit with experimental results.

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

Although it is not yet necessary to discard the crystal field model,^{8,11} this model assumes no mixing of J states by the crystal field and small intermediate coupling. Neither of these assumptions is strictly true for the Np^{3+} ion, as comparison of measured and calculated magnetic susceptibilities for $\text{Cs}_2\text{NaNpCl}_6$ indicates.¹² The predicted ordering of crystal field levels from first-order wave-functions¹³ for a $J = 4$ ion in an eight-fold cubic O site also predicts a nonmagnetic Γ_1 lowest level with Γ_4 and Γ_5 triplet levels higher in energy.¹³ Considering the environment of anion in a D_{8h} site not too different from an O site also yields a qualitative agreement with experiment.

The magnetic susceptibility of Pu^{3+} in $\text{KPu}(\text{COT})_2 \cdot 2\text{THF}$, $\mu_{\text{eff}} = 1.25\mu_B$, agrees with the free ion moment for Pu^{3+} with intermediate coupling taken into account¹⁴. However, it is difficult to rationalize three crystal field levels below 70°K for Np^{3+} in $\text{KNp}(\text{COT})_2 \cdot 2\text{THF}$ and a $\text{KPu}(\text{COT})_2 \cdot 2\text{THF}$ magnetic susceptibility that implies all crystal field levels for Pu^{3+} are below 2.2°K . It appears probable that there is an accidental agreement between the magnetic susceptibility of the ground crystal field level and the free ion value. Further experimental and theoretical

(12) M. E. Hendricks, E. R. Jones, Jr., J. A. Stone and D. G. Karraker, *J. Chem. Phys.*, **60**, 2095 (1974).

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

(14) N. Edelstein, H. F. Mollet, W. C. Easley and R. J. Mehlhorn, *J. Chem. Phys.*, **51**, 3281 (1969).

studies are considered necessary to explain the properties of these compounds adequately.

ACKNOWLEDGEMENTS

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TABLE I
X-Ray Diffraction Data For $\text{KM}(\text{COT})_2 \cdot 2\text{THF}$ Compounds

<u>$\text{KPu}(\text{COT})_2 \cdot 2\text{THF}$</u>		<u>$\text{KNp}(\text{COT})_2 \cdot 2\text{THF}$</u>	
<u>$d, \text{\AA}$</u>	<u>I^α</u>	<u>$d, \text{\AA}$</u>	<u>I</u>
8.35	M	8.16	W
6.52	S	6.69	M
5.53	S	5.53	M
4.71	W		
4.14	W	4.13	W
3.81	M	3.82	W
3.53	W	3.54	W
3.33	W	3.30	W
3.14	S	3.14	S
2.63	W		
2.45	W	2.45	W
2.27	W		
2.23	W	2.22	W
2.09	M	2.10	M
2.03	W		
1.92	W		
1.84	W	1.82	W
1.78	W		
1.71	W	1.73	W
1.65	W	1.65	W
1.57	W		
1.52	W		
1.40	W		

α . S, Strong; M, Medium; W, Weak.

TABLE II
 Partial X-Ray Diffraction Data for $\text{KM}(\text{COT})_2 \cdot \text{diglyme}$

<u>$\text{KCe}(\text{COT})_2 \cdot \text{diglyme}^a$</u>		<u>$\text{KPu}(\text{COT})_2 \cdot \text{diglyme}$</u>	
<u>2θ</u>	<u>I</u>	<u>2θ</u>	<u>I</u>
10.47	79		
10.81	244	10.84	S
11.37	100		
12.23	84		
12.52	60	12.44	S
12.63	404		
15.48	322	15.59	VS
16.43	141		
16.65	165	16.49	S
18.38	105	18.64	M
20.69	80	20.89	M
21.03	43		
21.26	55		
22.37	55	22.54	W
24.61	61	24.89	W
27.49	81	27.69	M
31.37	36	31.49	W
31.56	42		
31.84	46	32.09	W
33.85	22	33.69	VW
34.32	31		
34.57	14	34.69	VW
36.22	26		
36.77	22	36.59	W
36.77	22		
37.79	39		
39.03	21	38.94	W
40.80	20		
41.12	20	40.94	W

a. Calculated by computer from the crystal structure. See Reference 5.

TABLE III

Isomer Shifts of Neptunium(III)
And Neptunium(IV) Compounds At 4.2°K

Compound	Isomer Shift, ^a cm/sec
NpO ₂	-0.56
NpCl ₄	-0.34
NpAl ₂	0.00
NpCp ₄	+0.72
Np(COT) ₂ ^b	+1.94
NpCl ₃	+3.54
NpCp ₃ •3THF	+3.64
KNp(COT) ₂ •2THF	+3.92

^a. Relative to NpAl₂ at 77°K.

^b. COT = cyclooctatetraenyl ion, C₈H₈²⁻

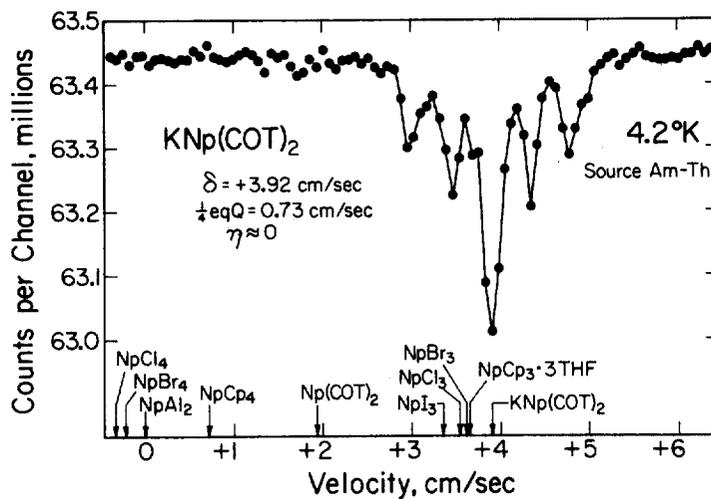


FIGURE 1. Mossbauer Spectrum of $\text{KNp}(\text{COT})_2 \cdot 2\text{THF}$

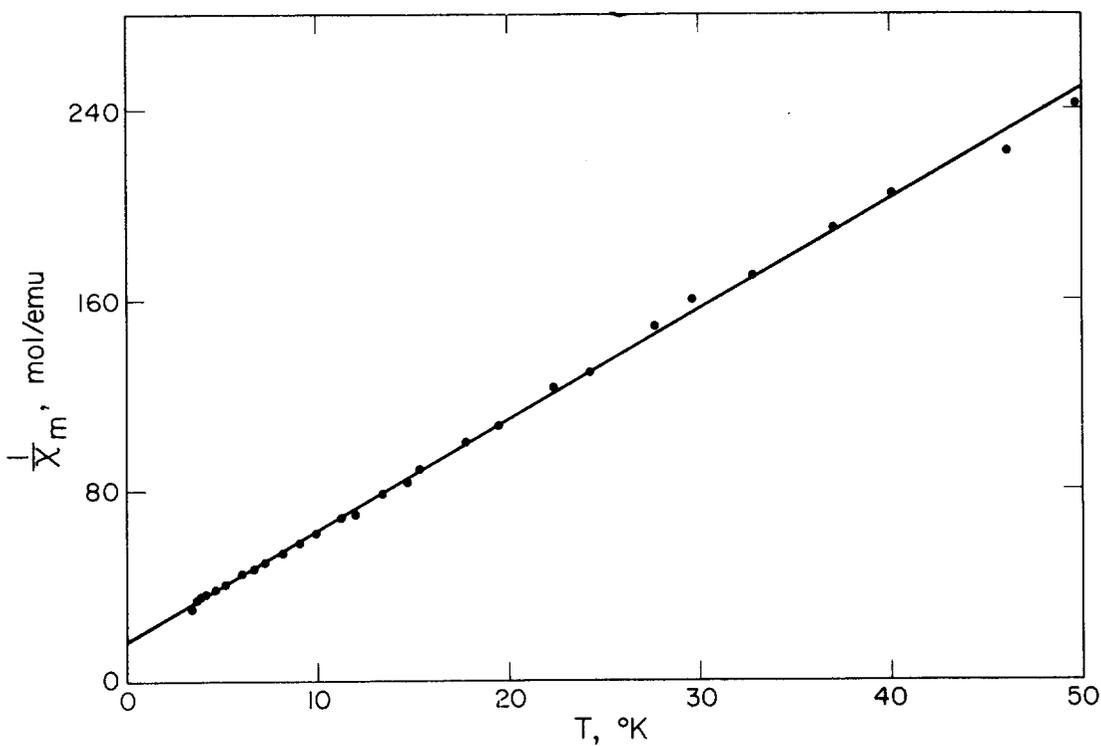


FIGURE 2. Inverse Magnetic Susceptibility of $\text{KPu}(\text{COT})_2 \cdot 2\text{THF}$

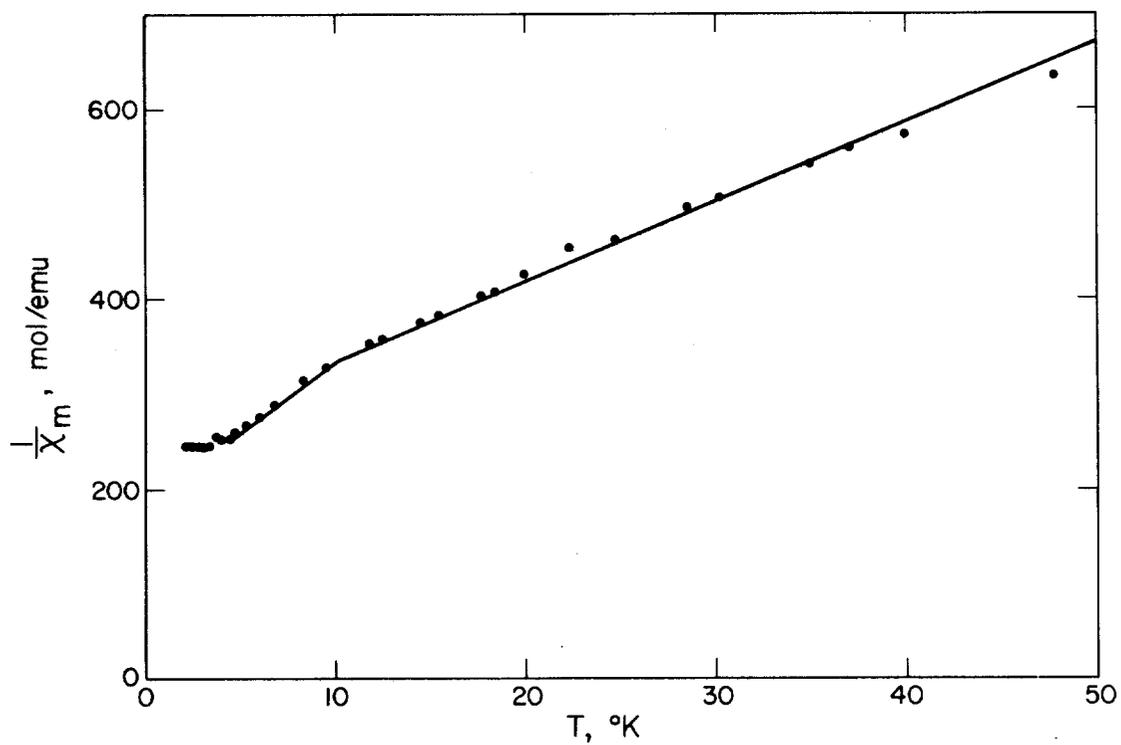


FIGURE 3. Inverse Magnetic Susceptibility Of $\text{KNp}(\text{COT})_2 \cdot 2\text{THF}$