

Lawrence Berkeley National Laboratory

Recent Work

Title

DIPOTASSIUM BIS-([8] ANNULENE) YTTERBIUM(II) AND BIS-([8] ANNULENE)CALCIUM

Permalink

<https://escholarship.org/uc/item/6jj9765j>

Author

Streitwieser, A.

Publication Date

1982-09-01



Lawrence Berkeley Laboratory

UNIVERSITY OF CALIFORNIA

Materials & Molecular Research Division

RECEIVED
LAWRENCE
BERKELEY LABORATORY

NOV 16 1982

LIBRARY AND
DOCUMENTS SECTION

Submitted to *Organometallics*

DIPOTASSIUM BIS-([8]ANNULENE)YTTERBIUM(II) AND
BIS-([8]ANNULENE)CALCIUM

Steven A. Kinsley and Andrew Streitwieser, Jr.

September 1982

TWO-WEEK LOAN COPY

*This is a Library Circulating Copy
which may be borrowed for two weeks.
For a personal retention copy, call
Tech. Info. Division, Ext. 6782.*



LBL-15018
c2

DISCLAIMER

This document was prepared as an account of work sponsored by the United States Government. While this document is believed to contain correct information, neither the United States Government nor any agency thereof, nor the Regents of the University of California, nor any of their employees, makes any warranty, express or implied, or assumes any legal responsibility for the accuracy, completeness, or usefulness of any information, apparatus, product, or process disclosed, or represents that its use would not infringe privately owned rights. Reference herein to any specific commercial product, process, or service by its trade name, trademark, manufacturer, or otherwise, does not necessarily constitute or imply its endorsement, recommendation, or favoring by the United States Government or any agency thereof, or the Regents of the University of California. The views and opinions of authors expressed herein do not necessarily state or reflect those of the United States Government or any agency thereof or the Regents of the University of California.

DIPOTASSIUM BIS-([8]ANNULENE)YTTERBIUM(II) AND BIS-([8]ANNULENE)CALCIUM

Steven A. Kinsley and Andrew Streitwieser, Jr.*

Materials and Molecular Research Division, Lawrence Berkeley Laboratory,
and Department of Chemistry, University of California
Berkeley, California 94720

Received

Summary: The dipotassium salts of the bis-[8]annulene dianion sandwich complexes of ytterbium(II) and calcium(II), a new class of [8]annulene sandwich compounds, have been synthesized and characterized. The identical IR spectra and similar x-ray powder patterns of these two compounds suggest that they have identical crystal structures and bond character.

We report a new class of bis-[8]annulene dianion¹ sandwich complexes, $K_2[M(C_8H_8)_2]$,² with the synthesis and characterization of the two complexes for $M = Yb(II)$, 1, and $M = Ca$, 2. Although many sandwich compounds are known for [8]annulene dianion and Ln(III) elements,³ only one class of complexes with Ln(II), $Ln(C_8H_8)$ ($Ln = Eu, Yb$), has been reported.⁴ Because of low solubility, the characterization of this class, thought to be polymeric, is limited to elemental analysis and infrared spectra.⁵ Consequently, 1 is the first well characterized complex of [8]annulene with a low-valent lanthanide.

1 and 2 were synthesized by a procedure similar to the reported syntheses of $Eu(C_5H_5)_2$ ⁶ and $Ln(C_8H_8)$.⁴ Two equivalents of cyclooctatetraene were added to a blue liquid ammonia solution of 2 equiv. of potassium and 1 equiv. of ytterbium or calcium metals. After the completion of the reaction (ca. 5 min at $-33^\circ C$), evaporation of the liquid ammonia left a pale green pyrophoric powder for 2 or a bright orange pyrophoric powder for 1. The orange color of 1 is characteristic of ytterbium compounds solvated with ammonia.⁷ When the solvated ammonia was removed, in vacuo, the color of the powder changed from orange to pink. When a 2:1:1 ratio of cyclooctatetraene:ytterbium:potassium was used in the liquid ammonia reaction, the bright blue ytterbium(III) compound, $K[Yb(C_8H_8)_2]$,⁸ 3, was obtained. Yields from these reactions were essentially quantitative.

The physical properties of the divalent ytterbium and calcium complexes are similar to those reported for the trivalent lanthanide complexes, $K[Ln(C_8H_8)_2]$.^{3a} 1 and 2 are thermally stable, showing no sign of decomposition when heated to $360^\circ C$ sealed under argon, or to $200^\circ C$, in vacuo. 3 is thermally unstable and is converted to 1 (and some unidentified decomposed material) when heated at $310^\circ C$ sealed under argon, or to $200^\circ C$, in vacuo (10^{-3} mm). A mass spectrum of 1 shows no m/e peak that can be attributed to

the ionization of the sandwich compound. 1 and 2 are insoluble in hydrocarbon solvents such as hexane, toluene and benzene but are soluble in ethers such as diethyl ether, tetrahydrofuran (THF), and 1,2-dimethoxyethane (DME). Like all of the lanthanide [8]annulene dianion complexes, the ytterbium and calcium complexes reported here exist as amorphous powders in the absence of coordinated ether molecules. Crystals of ether adducts were obtained by the slow diffusion of pentane into an ether solution of the complex. DME adduct is relatively stable and analyzes for one ether per potassium.⁹ Crystals of the THF adduct rapidly decompose to an amorphous powder and give an adequate but less satisfactory analysis.⁹ The ring proton resonance for the diamagnetic $K_2[Yb(C_8H_8)_2]$ in THF- d_8 appears as a sharp singlet ($\delta=5.47$ ppm) at $-50^\circ C$; the peak broadens as the sample tube is warmed to room temperature. The temperature dependence of the 1H -NMR spectrum of the ytterbium(II) complex is possibly due to electron or ligand exchange with traces of the paramagnetic $K[Yb(C_8H_8)_2]$. The ring proton resonance for $K_2[Ca(C_8H_8)_2]$ occurs as a sharp singlet ($\delta=5.49$ ppm) at $27^\circ C$.

1 is a strong reducing agent, reacting with O_2 (a stoichiometric amount in tetrahydrofuran), CCl_4 , C_8H_8 , and $U(C_8H_8)_2$ to form $K[Yb(C_8H_8)_2]$; the presence of the ytterbium(III) complex was indicated by its visible spectrum. When 1 equiv. of 1 was added to a THF solution of 1 equiv. of UCl_4 , the green solution turned brown and had the same visible spectrum as that reported for $Li[U(C_8H_8)_2]$.¹⁰ When exposed briefly to air, the brown solution turned green and had the visible spectrum of $U(C_8H_8)_2$.¹¹

The sandwich structure of the $K_2[M(C_8H_8)_2]$ salts is deduced by comparison of the infrared spectra of 1 and 2 with those of $U(C_8H_8)_2$ and $K[La(C_8H_8)_2]$ in the region $600-1000\text{ cm}^{-1}$ (Table 1). The infrared absorption bands have been assigned previously.¹²

The infrared spectra and x-ray powder patterns of 1 and 2 suggest that these two complexes have identical crystal structures.¹³ Since the ionic radii of Yb^{2+} and Ca^{2+} are nearly identical,¹⁴ this similarity of $\text{K}_2[\text{Yb}(\text{C}_8\text{H}_8)_2]$ and $\text{K}_2[\text{Ca}(\text{C}_8\text{H}_8)_2]$ is neither surprising nor unanticipated.¹⁵ These results further emphasize the lack of importance of the 4f orbitals in ytterbium(II) chemistry; e.g. the ring-metal interaction in 1 is undoubtedly wholly ionic. Further studies directed at the elucidation of the crystal structure of $\text{K}_2[\text{M}(\text{C}_8\text{H}_8)_2]$ and the reduction chemistry of 1 are in progress.

Acknowledgment. We are indebted to Dr. Alan Zalkin and Professor David Templeton for their assistance. This work was supported by the Director, Office of Energy Research, Office of Basic Energy Sciences, Chemical Sciences Division of the U.S. Department of Energy, under Contract No. DE-AC03-76SF00098.

Supplementary Material Available: Infrared and x-ray powder spectra for 1 and 2. Ordering information is given on any current masthead page.

References and Notes

- Controversy exists in naming sandwich organometallic actinide and lanthanide compounds of cyclooctatetraene; [8]annulene dianion is chosen here because this name properly describes the delocalization of charge in the ligand and also emphasizes the formal oxidation state of the metal. See Zalkin, A.; Templeton, D. H.; Luke, W. D.; Streitwieser, A., Jr. Organometallics 1982, 1, 618.
- The compound $K_2[Ce(C_8H_8)_2]$ has been reported, but no proof was given for a sandwich type structure. See ref. 3b.
- (a) Mares, F.; Hodgson, K.; Streitwieser, A., Jr. J. Organometal. Chem. 1970, 24, C68. Hodgson, K.; Mares, F.; Starks, D.; Streitwieser, A., Jr. J. Am. Chem. Soc. 1973, 95, 8650. (b) Greco, A.; Cesca, S.; Bertolini, G. J. Organometal. Chem. 1976, 113, 321. (c) DeKock, C. W.; Ely, S. R.; Hopkins, T. E.; Brault, M. A. Inorg. Chem. 1978, 17, 625. (d) Jamerson, F. D.; Masino, A. P.; Takats, J. J. Organometal. Chem. 1974, 65, C33.
- Hayes, R. G.; Thomas, J. L. J. Am. Chem. Soc. 1969, 91, 6876.
- The infrared spectrum of $Yb(C_8H_8)$ is reported in ref. 3c.
- Fischer, E. O.; Fischer, H. Angew. Chem. 1964, 76, 52.
- For examples see Howell, J. K.; Pytlewski, L. L. J. Less-Common Metals 1969, 18, 437 and ref. 4.
- 3 was not reported in the papers on the class of lanthanide compounds, $K[Ln(C_8H_8)_2]$, ref 3a. Crystallization from THF gives $K[Yb(C_8H_8)_2](C_4H_8O)_2$; λ_{max} (THF) 574 ($\epsilon=1400$). Anal. Calcd. for $C_{24}H_{32}O_2YbK$: C, 51.06; H, 5.71. Found: C, 51.37; H, 6.01; N, 0.04.
- Analyses: 2 -DME adduct; Calcd. for $C_{24}H_{36}O_4K_2Ca$: C, 56.88; H, 7.16; K, 15.43. Found: C, 57.11; H, 7.07; K, 16.7; N, 0.02. 2 -4THF adduct;

Calcd for $C_{32}H_{48}O_4K_2Ca$: C, 62.49; H, 7.87; K, 12.71. Found: C, 61.73; H, 7.40; K, 11.8; N, 0.02. Satisfactory analyses could not be obtained on the ytterbium(II) compound probably because of its extreme air sensitivity. Visible spectra (THF): λ_{max} 504 nm ($\epsilon=850$). The lack of absorbance in the near-IR at $\sim 10,000\text{ cm}^{-1}$ is consistent with Yb^{+2} . $\underline{2}$ has no absorbance in the visible; its pale green color is due to tailing from the ultraviolet.

10. Billiau, F.; Folcher, G.; Marquet-Ellis, H.; Rigny, P.; Saito, E. J. Am. Chem. Soc. 1981, 103, 5603.
11. Streitwieser, A., Jr.; Muller-Westerhoff, U.; Sonnichsen, G.; Mares, F.; Morrell, D. G.; Hodgson, K. O.; Harmon, C. A. J. Am. Chem. Soc. 1973, 95, 8644.
12. Aleksanyan, V. T.; Garbusova, I. A.; Chernyshova, T. M.; Todres, Z. V. J. Organometal. Chem. 1981, 217, 169.
13. The x-ray powder patterns of $K_2[M(C_8H_8)_2] \cdot (C_4H_{10}O_2)_2$ for Yb and Ca are essentially identical. The only non-coincident lines are very weak. The infrared and x-ray powder spectra are available as Supplementary Material.
14. Shannon, R. D. Acta Crystallogr. 1976, A32, 751.
15. The similarity in infrared spectra has been noted for $Yb(C_5H_5)_2$ and $Ca(C_5H_5)_2$. Fischer, E. O.; Fischer, H. J. Organometal. Chem. 1965, 3, 181.
16. Hocks, L.; Goffart, J.; Duyckaerts, G.; Teyssie, P. Spectrochim. Acta 1974, 30A, 907.

Table I. Comparison of infrared spectra^{a,b}

$U(C_8H_8)_2^c$	$K[La(C_8H_8)_2]^d$	$K_2[Yb(C_8H_8)_2]$ 1	$K_2[Ca(C_8H_8)_2]$ 2	assignment ^d
698 vs	680 vs	681 vs	683 vs	$\rho(CH)$, $A_{2\mu}$
746 s	740 m	739 m	740 m	$\nu(CC)$, $A_{2\mu}$
777 m	771 w			$\rho(CH)$, $E_{1\mu}$
792 m		795 w(br)	795 w(br)	
		879 s	879 s	
900 s	892 s	885 s	888 s	$\beta(CH)$, $E_{1\mu}$

^a vs, very strong; s, strong; m, medium; w, weak; br, broad. ^b nujol mulls.

^c ref. 16. ^d ref. 12.

Supplementary Material

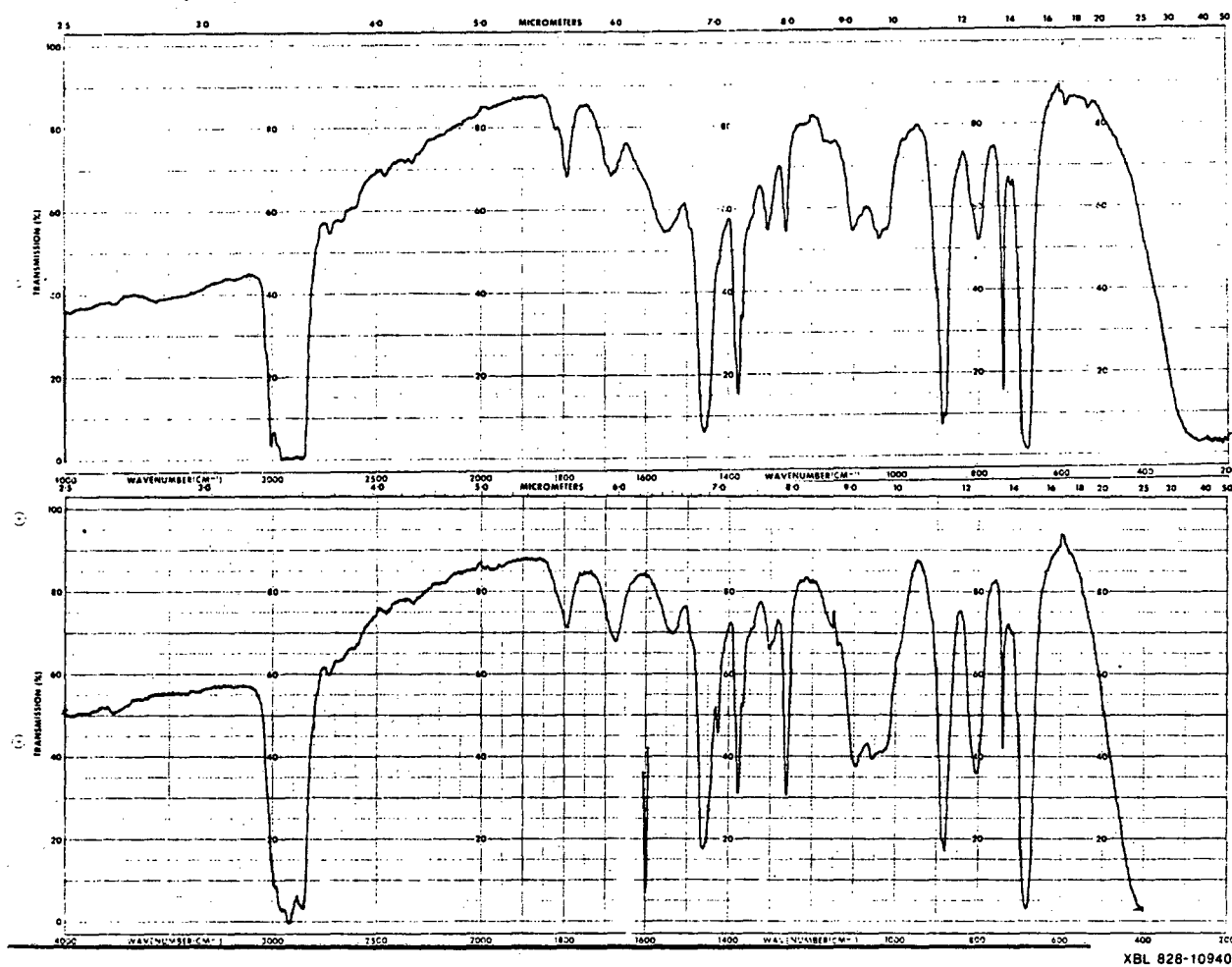
Fig. 1. Infrared spectra of $K_2[Ca(C_8H_8)_2]$ (top) and $K_2[Yb(C_8H_8)_2]$ (bottom). Both samples contain residual tetrahydrofuran (THF).

Fig. 2. Infrared spectra of $K_2[Ca(C_8H_8)_2] \cdot (THF)_4$ (top) and $K_2[Yb(C_8H_8)_2] \cdot (THF)_4$ (bottom).

Fig. 3. Infrared spectra of $K_2[Ca(C_8H_8)_2] \cdot (DME)_2$ (top) and $K_2[Yb(C_8H_8)_2] \cdot (DME)_2$ (bottom).

Table 2. X-ray powder data.

Figure 1



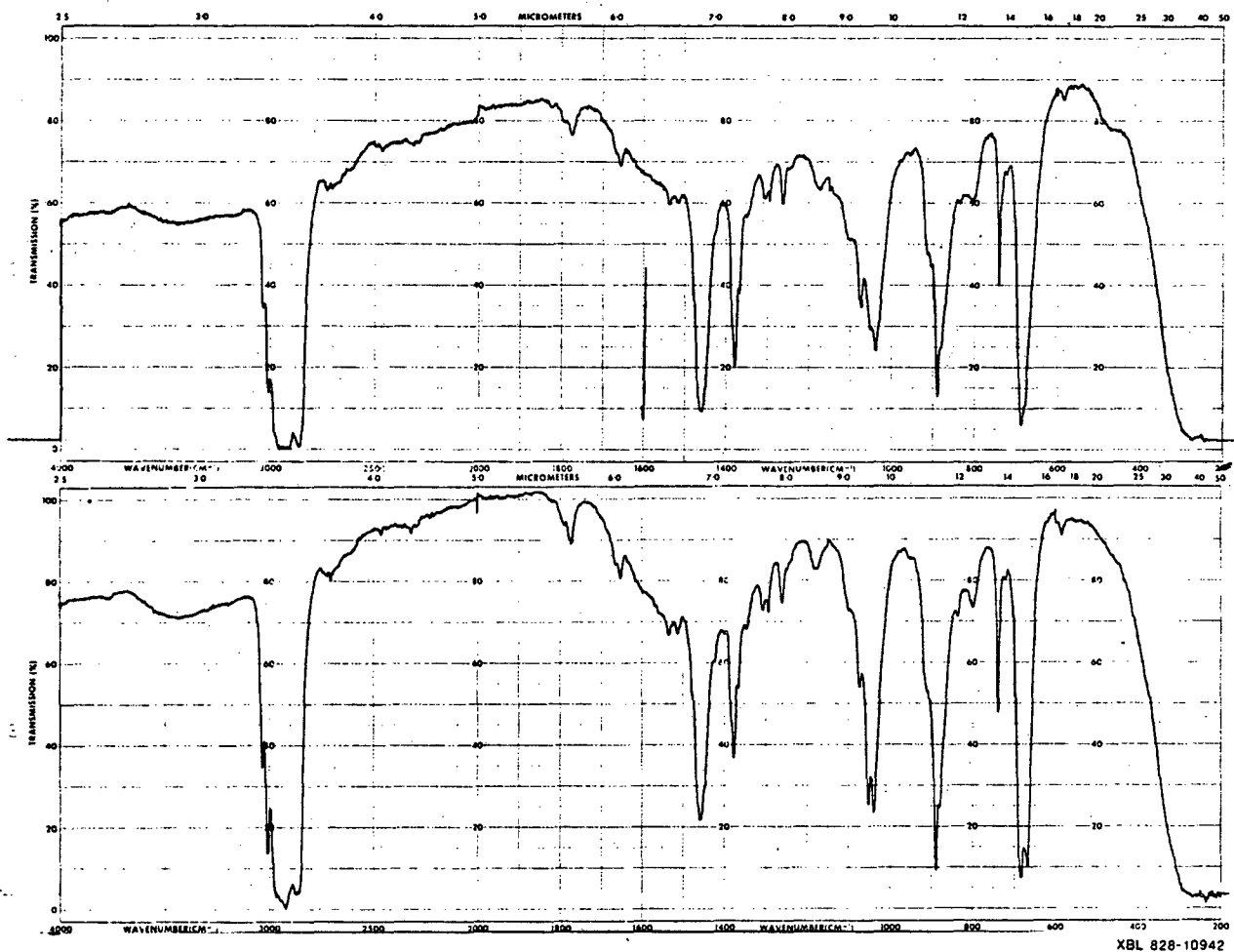
$K_2[Ca(C_8H_8)_2]$ - Top

$K_2[Yb(C_8H_8)_2]$ - Bottom

Note: samples contain residual THF.

XBL 828-10940

Figure 2

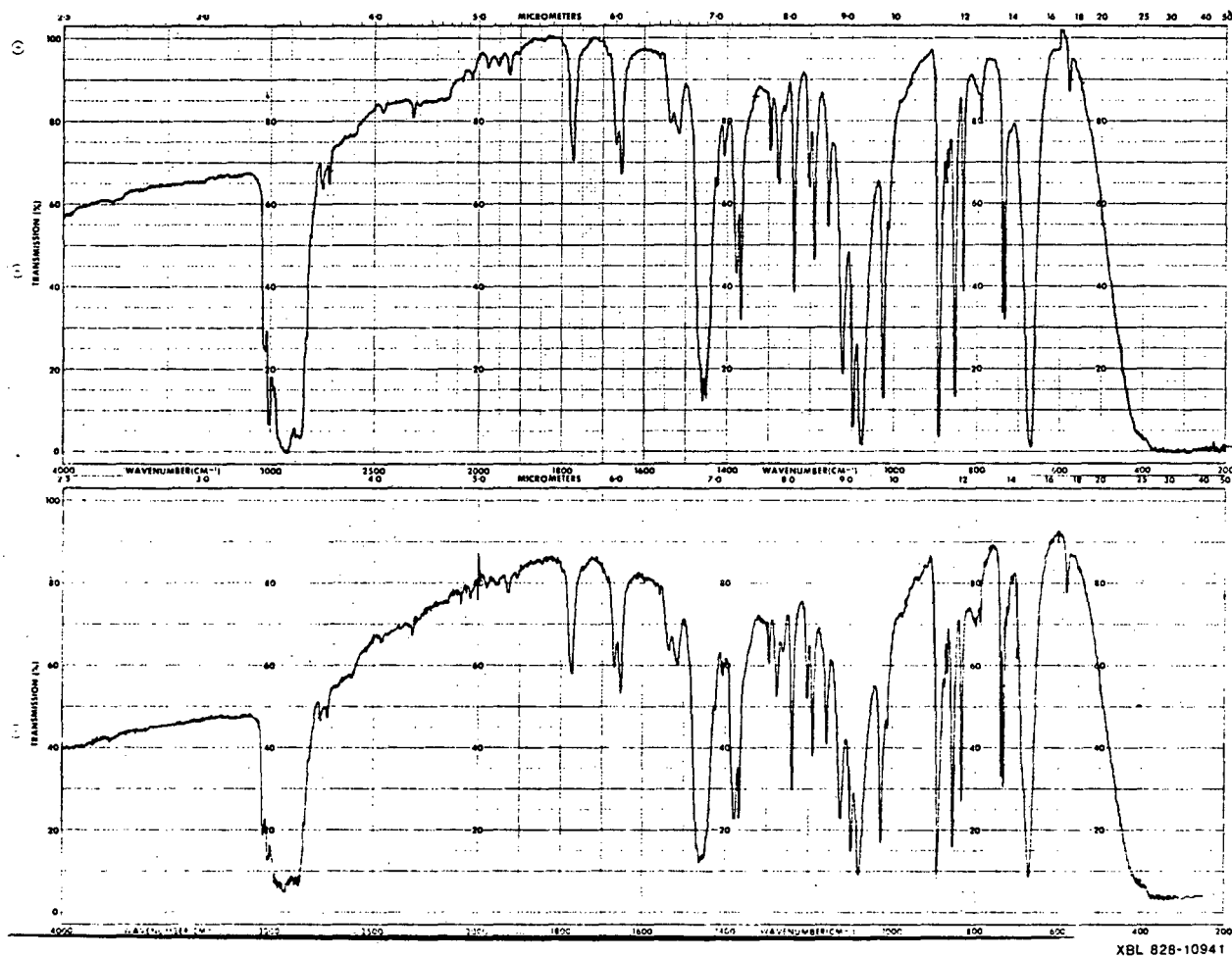


XBL 828-10942

$K_2[Ca(C_8H_8)_2] \cdot (THF)_4$ - Top

$K_2[Yb(C_8H_8)_2] \cdot (THF)_4$ - Bottom

Figure 3



XBL 828-10941

 $K_2[Ca(C_8H_8)_2] \cdot (DME)_2$ - Top $K_2[Yb(C_8H_8)_2] \cdot (DME)_2$ - Bottom

Table 2. X-ray powder data.

$K_2[Yb(C_8H_8)_2] \cdot (DME)_2$		$K_2[Ca(C_8H_8)_2] \cdot (DME)_2$	
$d(\text{\AA})$	i	$d(\text{\AA})$	i
9.826	w+		
8.801	w		
7.314	s-	7.329	s-
6.733	s	6.745	s
6.360	w+	6.405	w-
5.763	s-	5.772	s-
5.454	w-		
4.874	w+	4.901	w-
4.423	m	4.445	w
		4.306	w
4.152	w-	4.128	w-
4.072	w-	3.934	w-
3.850	m	3.850	m
		3.612	w-
		3.531	w-
3.427	w+	3.427	w
3.314	w-	3.308	w-
3.252	w-	3.252	w-
3.167	w	3.173	w+
3.102	w	3.097	w
2.971	m	2.983	w
2.943	m	2.938	w
2.876	w	2.882	w-
2.771	w-	2.780	w-
2.726	w-	2.714	w-

intensity (i) w = weak, m = medium, s = strong

This report was done with support from the Department of Energy. Any conclusions or opinions expressed in this report represent solely those of the author(s) and not necessarily those of The Regents of the University of California, the Lawrence Berkeley Laboratory or the Department of Energy.

Reference to a company or product name does not imply approval or recommendation of the product by the University of California or the U.S. Department of Energy to the exclusion of others that may be suitable.

TECHNICAL INFORMATION DEPARTMENT
LAWRENCE BERKELEY LABORATORY
UNIVERSITY OF CALIFORNIA
BERKELEY, CALIFORNIA 94720