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B. J. Bulkin [a] [b] , R. K. Rose [a] [c] & A. Santoro [a]

[a] Polytechnic Institute of New York, 333 Jay Street, Brooklyn, New York, 10021

[b] Polytechnic Institute of New York, 333 Jay Street, Brooklyn, New York, 10021

[c] Department of Physical Sciences, Kingsborough Community College of CUNY, Brooklyn, New York, 11235

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Synthesis and Thermal Properties of a Possibly Mesomorphic Palladium Chelate

B. J. BULKIN,† R. K. ROSE,‡[1] and A. SANTORO
Polytechnic Institute of New York, 333 Jay Street, Brooklyn, New York 10021

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The introduction of the *p*-alkoxy group into the model system of bis-(1-phenyl-1,3-butanedionato)-palladium(II) results in a modification of the thermal properties associated with the decomposition of Pd-beta-diketones and other palladium-oxygen coordination compounds. The potential mesomorphism of the bis(1*p*-octyloxyphenyl-1,3-butanedionato-palladium(II) complex prepared was difficult to establish, because of its darkening on heating.

INTRODUCTION

Mesomorphic compounds containing Na, K, Rb and Th have been reported by Vorlaender[3] and Walter;[4] some with Hg atoms by Urban[5] and Vorlaender;[6] with Si by Eaborn and Hartshorne;[7] with Si, Ge and Sn by Young *et al.*[8] In this paper we report the thermal properties of a new palladium chelate. The square planar geometry of the complex, combined with an anisotropic beta-diketone ligand comparable in geometry to *p*-octyloxybenzoic acid, make the new chelate a possible candidate for mesomorphism. The synthesis and properties of *trans bis*(1-*p*-octyloxyphenyl-1,3-butanedionato)palladium(II), or PdL_2 are reported here.

EXPERIMENTAL

The ligand—1-*p*-octyloxyphenyl-1,3-butanedione, or *p*-octyloxy-*bzac*—was prepared by the method described by Sabnis *et al.*[9] for the preparation of *p*-methoxy-*bzac*. The palladium chelate complex was prepared by the

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† Address correspondence to this author at Polytechnic Institute of New York, 333 Jay Street, Brooklyn, New York 10021.

‡ Present address: Department of Physical Sciences, Kingsborough Community College of CUNY, Brooklyn, New York 11235.

procedure outlined by Hon *et al.*[12] for Pd (bzac)$_2$ with slight modifications. A potassium salt was prepared by treating a large excess of the ligand (0.004 moles) in 10 ml. ethanol with ethanolic KOH stoichiometrically equivalent to the $PdCl_2$ (0.00137 moles), used as an aqueous suspension, stirring the mixture for 3 hours at room temperature, protected from light. Two palladium chelates corresponding to $Pd(C_{18}H_{25}O_3)_2$ were isolated from the reaction mixture. The properties of the first species isolated are described elsewhere.[1] It is the *cis* isomer of PdL_2. The *trans* isomer of PdL_2 separated from the reaction mixture after 24 to 48 hours, was washed with ethanol and water to remove excess unreacted ligand.

The PdL_2 *trans* is golden-yellow, mp. 235–235°(d). Elemental analysis calculated for $PdC_{36}H_{50}O_6$ is C, 63.10; H, 7.36; Pd, 15.52%; found: C, 63.04; H, 7.47; Pd, 15.24%. Molecular weight calculated is 685; found osmometrically (0.0066 molal soln.) in $CHCl_3$ 717 (ca. 5% error). The ultraviolet spectrum in CH_2Cl_2 has $\lambda_{max} = 310$ nm ($\varepsilon_{max} = 4.38 \times 10^4$) and $\lambda_{max} = 355$ nm ($\varepsilon_{max} = 3.48 \times 10^4$). The mid-infrared, Raman and NMR data

TABLE I

Spectral data of PdL_2, *trans*

NMR Data[a]				Infrared[b]	Raman[c]	Interpretation
δ	No.	H's	Interpret.	1620 s	1605 s	C=O str.
7.95 7.78	d	4	aromatic	1590 m		Ø ring str.
6.96 6.79	d	4	aromatic	1550 sh	1545	Ø ring str. + C=O str.
				1530 m	1515 s	mainly C=C str.
6.03	s	2	CH=CO		1420 m	CH_3 deg. deform.
					1370 w	CH_3 sym. deform.
				1250 s	1295 s	C—O str.; C—asym. str.
4.00	t		CH_2O	1220 m	1220 s	C—O str.; C—CH_3 bend.
					1175 m	C—H bend.
2.20	s	6	CH_3CO	840 m	830 m	Ø C—H out-of-plane bend (2 adjacent aromatic H)
1.33 0.90	m t br	30	$CH_3(CH_2)_6CH_2O$—Ø CH_3CH_2—	780 s		C—CH_3 str.

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[a] NMR peak positions are expressed in parts per million (ppm) as downfield shifts from internal TMS; abbreviations used: s = singlet; d = doublet; t = triplet; m = multiplet; br. = broad; Ø = phenyl.

[b] Mid-infrared spectra obtained as nujol mulls; abbreviations used: s = strong; sh = shoulder; m = medium; w = weak, str. = stretch; sym. = symmetric; deg. = degenerate; deform. = deformation.

[c] Raman spectra obtained on pure solid samples.

consistent with the structure assigned are summarized in Table I. Assignment of the *trans* and *cis* isomer of PdL_2 is based on the comparison of far infrared and Raman data and is detailed elsewhere.[1]

Differential thermal analysis (DTA) data are from the Dupont 900 DTA, using the differential scanning calorimeter (DSC) cell previously characterized by Baxter.[18] The DSC cell had been calibrated as described by Hoyer and Nevin.[17] The heating rate was programmed at 10 degrees per minute, at a sensitivity of either 0.1 or 0.2 degree per inch; cooling was achieved by disconnecting the heater and allowing the instrument to cool at an undetermined rate.

NMR spectra were obtained at 60 MHz, using a Varian Associates Model A-60 Analytic Spectrophotomoter. Infrared spectra were obtained on a Perkin Elmer Model 521 dual grating spectrophotometer. Raman spectra were taken with a Spex Industries Model 1401 Spectrometer. A Cary Recording Spectrophotometer Model 14-R was used to record ultraviolet spectra.

RESULTS

DTA was used to compare the thermal behavior of PdL_2 with other palladium chelates containing Pd—O bonds. The reference compounds show no endotherms prior to decomposition. The DTA of palladium(II) acetate shows decomposition at 200°C (±2°) (reported[10] to melt at 205° with decomposition). The DTA of bis(acetylacetonato)palladium(II) or $Pd(acac)_2$ shows decomposition near 200°. Its melting point cannot be determined, but its decomposition with charring above 180° has been reported.[11] The DTA of bis(1-phenyl-1,3-butanedionato)palladium(II) or Pd $(bzac)_2$ prepared in this laboratory, shows decomposition near 200°. Its melting point has not been previously reported.[13,14] Nesmeyanov *et al.*[15] reported that Pd(3-phenyl-acac)$_2$ melts with decomposition at 213–216°C.

Introduction of the *p*-octyloxy chain into $Pd(bzac)_2$ changes the thermogram markedly. Figure 1 shows the thermogram of PdL_2 with two small endotherms (0.4 ± 0.1 cal/g) at 178 ± 2 and 192 ± 3°, preceding the main endotherm (4.0 ± 0.4 cal/g) at 222 ± 3°, with decomposition following above 250 ± 5°C. If PdL_2 is heated above 220°, decomposition follows, and the endotherms observed at ca. 180 and 195° are no longer reversible. However, if PdL_2 is heated to only 200° and then cooled, exotherms are observed, and this reversibility can be repeated.

The region above 150° will be considered first, as shown in Figure 1. Curve A shows two small endotherms on first heating; cooling curve B shows a corresponding exotherm near 160°, with some supercooling; on

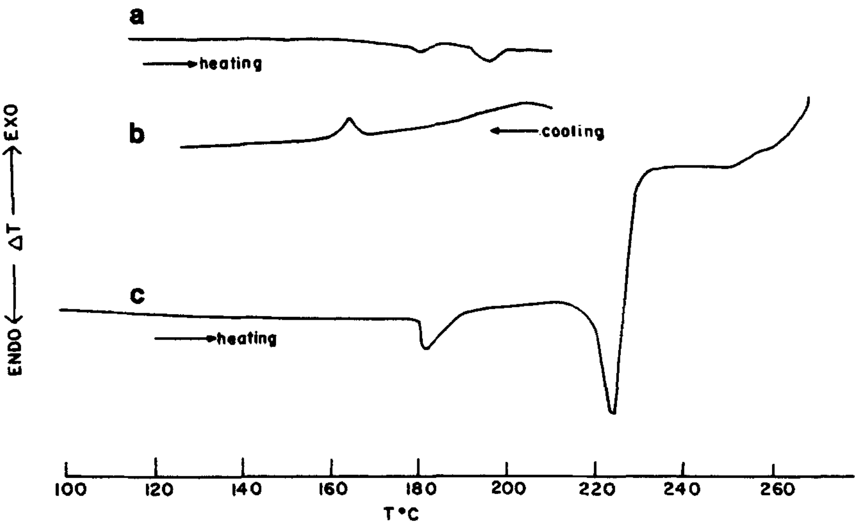

FIGURE 1 Thermogram of PdL_2 in higher temperature region. A (upper) Curve obtained on first heating of the sample. B (middle) Cooling curve obtained following curve 2A. Note that sample was not heated above 210 . C (lower) Reheating of same sample as in 2A and B.

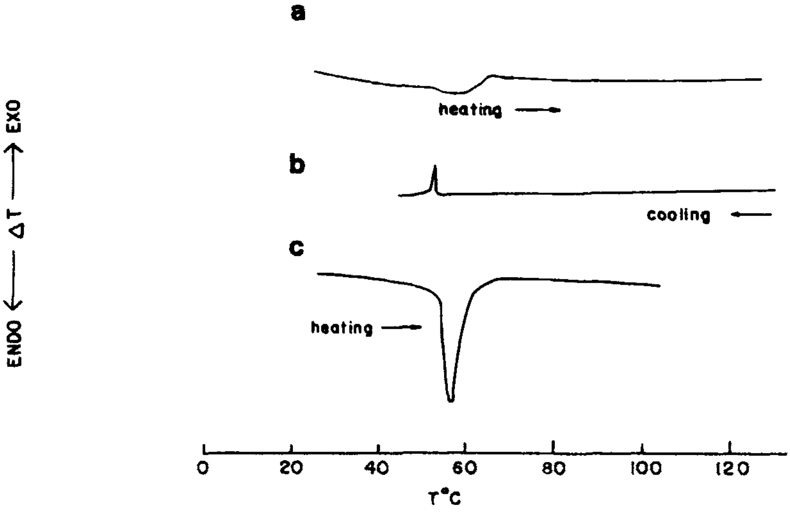

FIGURE 2 Thermograms of PdL_2 in lower temperature region. As in Figure 1, the upper curve is the first heating of the sample, middle curve is cooling, and lower curve reheating.

reheating curve C shows the two smaller endotherms coalesced into a larger one near 182°C. Curve C also shows the final melting endotherm near 225°, with decomposition following.

In another experiment at lower sensitivity (Figure 2) the region near 60° is shown, with only a small endotherm on first heating at 55 ± 3°. This endotherm becomes more pronounced during reheating ((1.8 ± 0.2 cal/g) curve 2-C). Cooling curve 2B shows the corresponding exotherm near 50°C. These endotherms and exotherms are also reproducible on second and third reheating and cooling.

Observations of samples of PdL_2 upon heating in a capillary tube suggest mesomorphism. Near 170°C the solid becomes translucent, shrinks away from the walls, with some "droplets" clinging to the capillary. These changes might indicate a mesophase, or a change from an opaque to a translucent solid. Thin films of PdL_2 were also examined under a polarizing microscope, with heating from ambient temperature to 280°C. Similarly, films of known mesomorphic substances with solid-solid transitions were examined. Above 170°C PdL_2 gradually changes from a light yellow to a dark brown color. Although this darkening makes observations difficult, the PdL_2 complex did not exhibit the optical anisotropy expected of a mesogen.

DISCUSSION

The endotherm near 60° appears to be a solid-solid transition, perhaps similar to that observed in *p*-octyloxybenzoic acid at 75°. It has been proposed[16] that the 75° transition involves the onset of chain rotation, or a change in the angle of tilt within the planes of the molecule.

Although microscopic examination does not confirm mesomorphism, the combined DTA and capillary tube observation suggest it. The endotherm near 225° is attributed to melting, but those near 178 and 195° are either solid-solid transitions, or mesomorphic changes difficult to detect microscopically because of darkening accompanying heating. One might speculate that the color changes observed several degrees below the 178° endotherm are due to melting of possible oligomeric forms of PdL_2, or that they represent changes in crystal stacking due to metal-metal interactions.

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References

1. Taken in part from the Ph.D. Thesis of Rose K. Rose, City University of New York (1976).
2. W. Kast, *Landolt-Boernstein Zahlenwerete und Funktionen*, 6th Ed., Springer-Verlag, Berlin, Vol. II, Part 2a, p. 266 (1960).
3. D. Vorlaender, *Chem. Ber.*, **43**, 3120 (1910).
4. R. Walter, *Chem. Ber.*, **59**, 962 (1926).
5. R. Urban, Dissertation, Universitaet Halle (1922).
6. D. Vorlaender, *Chemische Kristallographie der Fluessigkeiten*, Akademische Verlagsgesellschaft, Leipzig (1924).
7. C. Eaborn and N. H. Hartshorne, *J. Chem. Soc.*, 549 (1955).
8. W. R. Young, I. Haller, and D. C. Green, *Molecular Crystals and Liquid Crystals*, **13**, 305 (1971).
9. S. S. Sabnis, K. D. Kulkarni, and C. V. Deliwala, *J. Sci. Industry. Res.*, **17A**, 421 (1958).
10. T. A. Stephenson, S. M. Morehouse, A. R. Powell, F. P. Heffer, and G. Wilkinson, *J. Chem. Soc.*, 3632 (1965).
11. A. A. Grinberg and L. K. Simonova, *Zh. Priklad. Khim.* (in Russian), **26**, 880 (1953).
12. P. K. Hon, C. E. Pfluger, and R. L. Belford, *Inorg. Chem.*, **6**, 730 (1967).
13. E. A. Shugam, L. M. Shkol'nikova, and V. V. Zelentsov, *Zh. Strukt Khimii* (in Russian), **7**, 128 (1966).
14. P. R. Singh and R. Sahai, *Aust. J. Chem.*, **22**, 263 (1969).
15. A. N. Nesmeyanov, A. Z. Rubezhov, S. P. Gubin, and Z. B. Mitroshina, *Izv. Akad. Nauk SSSR, Ser, Khim.* (in Russian) 739 (1966).
16. A. J. Herbert, *Trans. Faraday Soc.*, **63**, 555 (1967).
17. H. W. Hoyer and S. Nevin, *Analytical Calorimetry*, Vol. 3, Plenum Press, New York (1974).
18. R. S. Baxter, *Thermal Analysis*, Vol. I, edited by R. F. Schwenker and P. D. Garn, Academic Press, Inc., New York (1969).