Table II. Frequencies (cm⁻¹) of the Major Resonance-Enhanced Raman-Active Modes of the Retinal Isomers, in CCl₄ Solution, with Assignments in Terms of the Band Model

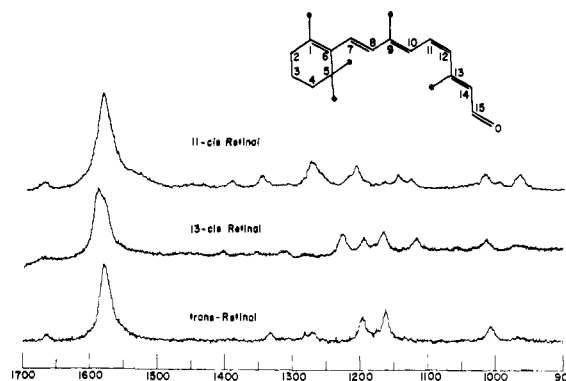| 11-Cis	Trans	13-Cis	Assignment
965	965	968	Chain C–H bending
999	1006	1010	C–C stretch of C(n)–CH₃; $n = 9, 13$
1018			
		1116	
1126			
1145	1160	1163	
1155			
1207	1198	1192	Admixed band of chain C–C stretch and C–H bend
		1224	
	1268		
1272	1278	1278	
	1327	1310	
1343		1352	
1388	1386	1401	
1431	1445	1450	C–H bend of protons on methyls bound to C(9) and C(13)
1448			
1523			Ethylenic band, mainly chain C=C stretch
	1546	1552	
		1575 (sh)	
1577	1578	1584	

Figure 1. Raman spectra of three retinal isomers, 3.5 mM in CCl₄. The spectra of the 11- and 13-cis isomers were taken at an excitation frequency of 17,602 cm⁻¹ (5680 Å). The trans isomer spectrum was obtained with 15,455-cm⁻¹ (6471 Å) krypton-laser radiation. Scanning speed 20 cm⁻¹/min, integration time ∼1 sec, spectral slit ∼2 cm⁻¹. For this set of spectra there was no analyzer in the scattered beam; the incident radiation was polarized perpendicular to the scattering plane, and polarization measurements showed all lines essentially corresponding to diagonal Raman tensors. The structural formula given in the figure represents the conventional 11-cis, 12-s-trans isomer, which, according to recent X-ray data, is not that encountered in the solid, and which is probably only one of the possible equilibrium configurations in solution at room temperature (see W. Sperling, Nature (London), 232, 187 (1971); B. Honig and M. Karplus, ibid., 229, 558 (1971)).

vidual band depends on interactions involving the parent vibration of the band. Clamped boundary conditions dictate a stationary pattern of vibrational modes, with an integral number of half-wavelengths ($\lambda/2$) matching the length of the conjugated segment of the chain. The bands derived from the C–C stretching and C–H in-plane bending parent modes are located in the 900–1300-cm⁻¹ range, while the modes of the ethylenic band are in the 1400–1600-cm⁻¹ range. The observed spectra of the various cis isomers reveal frequency shifts and large relative intensity changes in the 1000–1300-cm⁻¹ range. In terms of the model, these features probably are determined by the position of the cis kink relative to the maxima of the modes which have zero amplitude at the end points of the chain. Cis isomerization may also remove the degeneracy of modes having equal frequencies and diverse wave vectors. Such degeneracies pertain to a zero-slope (flat) segment in the dispersion curve ($\bar{\nu} = \bar{\nu}(q)$; $q = 2\pi/\lambda$) of the band. A flat segment was calculated for the C–C stretching and C–H in-plane bending band near its frequency minimum which is at ∼1160 cm⁻¹ in trans-retinal.[9] The observed splitting of this line in the spectrum of 11-cis-retinal (Figure 1 and Table II) indicates that in trans-retinal it was at least triply degenerate.

An important result particular to the 11-cis isomer is the splitting of the lines which in trans-retinal are at 1010 and 1440 cm⁻¹. The 1010 mode has been assigned to the stretching of the C–C bond which connects chain carbons 9 and 13 with their respective methyl groups (Figure 1). The 1440-cm⁻¹ mode, assigned to C–H bending within each methyl group, is resonance enhanced probably because of degeneracy with modes of the ethylenic band. In trans-retinal the methyl groups at positions 9 and 13 are unhindered, and their respective group vibrations are probably degenerate. The removal of this degeneracy in 11-cis-retinal by the hindrance of the methyl group attached to carbon 13 is a possible explanation of the splitting observed around 1010 and 1440 cm⁻¹. However, recent in-

(9) D. Gill and L. Rimai, manuscript in preparation.

vestigations[10,11] indicate that at room temperature 11-cis-retinal in solution exists as an equilibrium mixture of two conformations which differ in the C₁₂–C₁₃ torsional angle (12-s-trans and 12-s-cis). Hence it is also possible that the splitting of the 1010- and 1440-cm⁻¹ Raman lines results from the different frequencies contributed by the two conformations.

The question of whether the hindrance is relaxed at low temperatures in a glassy phase (as indicated by the rise in $\epsilon(\lambda_{max})$[4]) could not be tested in EPA glass because the Raman lines of the solvent masked the fingerprint modes of retinal. The ethylenic mode was observable and did not shift upon cooling to −125°.

In summary, we confirm the uniqueness of the Raman spectrum of each of the common mono-cis-retinal isomers, and thus indicate the usefulness of the spectra for monitoring isomerization reactions. The identification of the stereoisomers can be accomplished by relatively rapid scanning in the limited range of 1100–1300 cm⁻¹, even with far-red excitation (6740 Å). This would make possible the Raman study of rhodopsin and its less-stable bleaching intermediates.

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Molecular Structure of Palladium and Platinum Bis(ethylene-1,2-dithiolene). A Novel Metal–Metal Bonded Dimer

Sir:

The unusual properties and molecular structures of 1,2-dithiolene complexes have received considerable
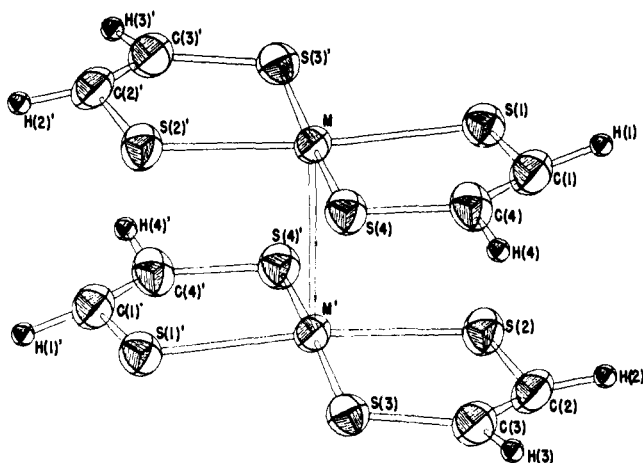
Figure 1. Molecular structure of $(MS_4C_4H_4)_2$, M = Pd, Pt.

attention in the recent past.[1] A large number of 1,2-dithiolene complex crystal structures have been reported. Most of these contain monomeric units with the central metal atom surrounded by four sulfur atoms in a near-perfect square-planar arrangement. Also, structures containing dimeric units with the metal surrounded by five sulfur atoms have been described for complexes of some of the lighter transition metals.[2] We report here the first examples of dimeric 1,2-dithiolene complexes with direct metal–metal bonding. The unique structure of these complexes has important implications to both the understanding of bisdithiolene structures and to metal–metal bonding in coordination compounds.[3]

The complexes studied are derivatives of the ethylene 1,2-dithiolate ligand and have the empirical formula $MS_4C_4H_4$ (M = Ni, Pd, Pt). They were prepared by iodine oxidation of the salts $(Pr_4N^+)(MS_4C_4H_4^-)$, using the method of Hoyer, et al.[4] The synthesis and some properties of $NiS_4C_4H_4$ have been discussed previously,[5] but $PdS_4C_4H_4$ and $PtS_4C_4H_4$ are reported here for the first time.

Marked differences in the electrical conductivity and X-ray powder diffraction patterns, of $NiS_4C_4H_4$ on the one hand, and $PdS_4C_4H_4$ and $PtS_4C_4H_4$ on the other,[6] led us to single-crystal X-ray diffraction studies on each of the three neutral complexes. Single crystals of each compound were grown from CS_2 solution by slow cooling or evaporation. Complete three-dimensional single-crystal X-ray diffraction data were taken with Cu Kα radiation using a GE490 automated diffractometer. The structures were solved by means of Patterson and Fourier syntheses and refined by least squares.

The details of the structure of $NiS_4C_4H_4$ are in agreement with the preliminary data of Höhne, et al.,[7] and

the complete structural investigation of Smith.[8] This compound crystallizes in the monoclinic space group $P2_1/n$ with $a = 10.90$, $b = 6.00$, $c = 6.47$ Å, $\beta = 93.9°$, $Z = 2$; the units are monomeric and have no exceptionally close intermolecular contact.

$PtS_4C_4H_4$ and $PdS_4C_4H_4$ are isostructural and crystallize in the monoclinic space group $P2_1/n$. Crystal data for $PdS_4C_4H_4$ are $a = 9.916$, $b = 11.788$, $c = 6.472$ Å, $\beta = 92.21°$, $Z = 4$; for $PtS_4C_4H_4$ $a = 9.97$, $b = 11.87$, $c = 6.47$ Å, $\beta = 92.0°$, $Z = 4$. At the present stage of refinement, $R = 0.064$ (F basis) for $PdS_4C_4H_4$ (1349 independent reflections) and $R = 0.092$ for $PtS_4C_4H_4$ (1116 independent reflections). The molecular structure of the $MS_4C_4H_4$ (M = Pd, Pt) complexes, shown in Figure 1, consists of two essentially planar $MS_4C_4H_4$ units joined by a direct metal–metal bond. In the Pd structure, each metal atom is drawn inward from the plane of four S atoms by 0.12 Å to give a Pd–Pd distance of 2.79 Å; the corresponding Pt–Pt distance is 2.77 Å. These distances are comparable to those observed in the metal and are among the shortest ever observed in coordination complexes of Pd and Pt.[9] The eight sulfur atoms of the dimer form a slightly distorted cube with the S–S distances between $MS_4C_4H_4$ units (average 3.026 Å) slightly shorter than those within the $MS_4C_4H_4$ units (average 3.253 Å).

This novel molecular arrangement is quite distinct from the laterally displaced dimeric structures exhibited by several other bisdithiolene complexes, where interactions between the dimer halves are of the metal–sulfur type.[2] Certain features of this structure, such as the approximately square arrangement of sulfur atoms at the faces of the S_8 polyhedra and the relatively short S–S distances, bear resemblance to the trigonal-prismatic geometry found for several of the tris-1,2-dithiolene complexes, where S–S bonding is believed to be important in stabilizing the molecular structure.[10]

Preliminary molecular weight and mass spectral data for $PtS_4C_4H_4$ indicate a monomeric structure for this complex both in solution and in the vapor state. The detailed results of these studies and complete structural information will be reported subsequently.

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Physical Parameters and Crystal Structure of a Unique Pentacoordinate Copper(II) Hippurate Dimer

Sir:

Authentic five-coordinate complexes of the first-row transition metals are being reported with increasing frequency.[1-3] In general, they are formed with simple monoatomic or diatomic ligands such as halide or carbonyl, or they are formed by polydentate ligands which

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