Table I. Threshold Temperature (T_i) and the Enthalpy Changes Associated with the Endothermic Transitions for Copper(II) and Nickel(II) Complexes with *N,N*-Diethylethylenediamine (L)

Complex	T_i,[a] °C	ΔH,[b] kcal mol^{-1}
$CuL_2(BF_4)_2$	15	2.40 ± 0.16
$CuL_2(ClO_4)_2$	35	2.13 ± 0.16
$CuL_2(NO_3)_2$	149	4.18 ± 0.20
$NiL_2(BF_4)_2$	94	1.37 ± 0.06
$NiL_2(ClO_4)_2$	110	1.59 ± 0.06

[a] T_i refers to the temperature at which the pen deflects from the base line; reported values refer to measurements carried out at the temperature scan rate of 1°/min. [b] The reported heat changes are the mean of at least six measurements carried out in the sensitivity range of 4 mcal (full scale deflection)$^{-1}$ sec^{-1}.

identical with that measured spectroscopically (Figures 1 and 2). The endotherm is exactly mirrored by the exotherm obtained by reverse dsc, *i.e.*, upon cooling, and the measured heat changes agree within experimental error (±4%). The transition can be repeated indefinitely by successive heating and cooling cycles, as long as the decomposition temperature is not attained. Thermogravimetric analysis shows that there is no weight change upon heating.

Both nickel and copper complexes are basically square planar with the tertiary nitrogen atoms in mutually trans positions. The anions may approach the cation along the fourfold axis, as shown by structure determinations on analogous complexes.[8,9] The energy of the d-d transition reflects, to a first approximation, changes in the equatorial environment. Increasing temperature shifts the band ($^1A_{2g} \leftarrow {}^1A_{1g}$ for $Ni(dieten)_2^{2+}$, D_{4h} symmetry[10]) to lower energy, suggesting a weakening of the M-N bond. Along with this weakening there is increasing axial perturbation. This is clearly shown in the ir spectra where bands due to "coordinated" anion appear at high temperature.

The progressive decrease in the distance between the anion and cation is accompanied by a progressive increase in the nonbonding interaction between the anion and the ethyl groups of the tertiary nitrogen atoms. With the easily deformable anions Br^-, $CdBr_4^{2-}$, I^-, AgI_2^-, PbI_3^-, and HgI_4^{2-} this process can occur continuously. With the less easily deformable anions BF_4^-, ClO_4^-, and NO_3^- the process is discontinuous because there is an energy barrier of a steric nature which must be exceeded by the change in bonding energy resultant upon anion coordination. This energy change is reflected in the dsc measurements. The transition temperatures of the nickel complexes are some 70° higher than for the corresponding copper complexes. The predicted transition temperature for $Ni(dieten)_2(NO_3)_2$ is therefore *ca.* 220°, that is, higher than the decomposition temperature. This explains why $Ni(dieten)_2(NO_3)_2$ shows no sharp transition temperature even though the anion is not easily deformable.

The energy of the endothermic transition, ΔH, correlated well with the spectral energy change as measured by the red shift $\Delta\nu$. For example both ΔH and $\Delta\nu$ are higher for copper than for nickel. If the $\Delta\nu$ value is corrected into energy units, it is seen to be 50 ± 5% of the ΔH value in the copper complexes. Clearly factors additional to the change in ligand field energy are included in the measured ΔH change. One such factor would be a phase change associated with the spectral change, and in fact X-ray measurements show that the two forms of $Cu(dieten)_2(ClO_4)_2$ are not isomorphous.[11]

Experimental Section

Materials. *N,N*-Diethylethylenediamine, Fluka purum, was distilled under reduced pressure and the middle fraction was used in the preparation of complexes. Copper(II) complexes, red isomers, were obtained as described.[2,4] Furthermore reaction of equimolecular amounts of $Cu(NO_3)_2 \cdot 6H_2O$ and ligand in ethanolic solution at 60° gives the less stable blue form of $Cu(dieten)_2(NO_3)_2$. The blue isomer slowly converts into the red species. The transformation was nearly complete in 2 months.

Some of the nickel(II) complexes were previously reported.[5] In general they were obtained by reaction of stoichiometric amounts of the amine and the appropriate nickel(II) salt in butanol at room temperature, followed by recrystallization from the same solvent. Anhydridization of the solvent and of the reactants is required in order to prevent hydrolysis. In the case of complexes with X^- = AgI_2^-, PbI_3^-, $^1/_2\ HgI_4^{2-}$, and $^1/_2\ CdBr_4^{2-}$, an ethanol solution of the halo complex was obtained dissolving the metal halide in a large excess (1:5, 1:10) of the sodium halide (*e.g.*, AgI + NaI). The complex was obtained by mixing the latter solution with an ethanolic solution of nickel(II) chloride and diamine. All of the complexes were analyzed for C, H, and N. In the case of soluble compounds, copper and nickel contents were determined electrolytically. The analysis gave satisfactory results.

Calorimetric Measurements. Calorimetric measurements were carried out with a differential scanning calorimeter, Perkin-Elmer DSC-1B. The instrument was connected to a pen recorder (Speedomax W, Leeds and Northrup) and the heat was measured from the area traced by the pen. The instrument was calibrated in the sensitivity range of 4 mcal (full scale deflection)$^{-1}$ sec^{-1}, at the temperature scan speed chosen, from the heat of fusion of several substances: indium, furnished by Perkin-Elmer, ΔH_f = 0.781 1 kcal mol^{-1};[12] tin, Schuchardt 99.999%, ΔH_f = 1.720 kcal mol^{-1};[12] zinc, Schuchardt, 99.999%, ΔH_f = 1.595 kcal mol^{-1};[13] sodium nitrate, Erba ACS, ΔH_f = 3.76 kcal mol^{-1}.[12] The instrument constant separately obtained was reproducible within the 4% and the mean value was used. Calorimetric measurements both on standard samples and on thermochromic compounds were carried out at different temperature scan rate (from 1 to 8°/min) but the heat measured was the same to within the experimental error (4%). Dry nitrogen flowed through the system at a rate at 30 ml/min. Samples (4-8 mg) were weighed on a Cahn gram electrobalance.

Spectral Measurements. Visible reflectance spectra (filter paper technique) were recorded on a Beckman DK-2A spectrophotometer at various temperatures. The temperature of the sample was determined with a thermocouple. Infrared spectra were recorded on a Perkin-Elmer Model 457 grating spectrophotometer employing mulls in Nujol supported on CsI plates. In recording spectra at higher temperatures the accessory furnished by Perkin-Elmer Bodenseewerk was used. The temperature scale (50-200°) was calibrated from the fusion of chosen organic samples.

Registry No. $Cu(dieten)_2(BF_4)_2$, 52646-61-4; $Cu(dieten)_2(ClO_4)_2$, 52646-62-5; $Cu(dieten)_2(NO_3)_2$, 52646-63-6; $Ni(dieten)_2(BF_4)_2$, 52613-62-4; $Ni(dieten)_2(ClO_4)_2$, 42534-35-0; $Ni(dieten)_2(NO_3)_2$, 52613-63-5.

(8) A. McPherson, M. G. Rossmann, D. W. Margerum, and M. R. James, *J. Coord. Chem.*, 1, 39 (1971).

(9) S. C. Nyburg and J. S. Wood, *Inorg. Chem.*, 3, 468 (1964).

(10) C. J. Ballhausen and A. D. Liehr, *J. Amer. Chem. Soc.*, 81, 588 (1959).

(11) C. E. Pfluger and J. W. Eihausen, private communication cited in ref 3.

(12) "Handbook of Chemistry and Physics," 50th ed, The Chemical Rubber Co., Cleveland, Ohio.

(13) *Nat. Bur. Stand.* (*U. S.*), *Circ.*, No. 500 (1952).

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Spectroscopic Studies of Dialkyltellurium Tetraiodides

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The first dialkyltellurium tetraiodide, $(CH_3)_2TeI_4$, was reported in 1921 by Vernon.[1] Subsequent workers have pre-

Table I. Proton Nmr Spectra[a]

Compd	$\delta(\text{-CH}_2\text{Te})$	$\delta(\text{-CH}_2)$	$\delta(\text{-CH}_3)$	$J_{^1\text{H}-^{125}\text{Te}}$
$(CH_3)_2TeI_2$	3.37			26
$(CH_3)_2TeI_4$	3.35			26
$(C_2H_5)_2TeI_2$	3.57		1.77	22
$(C_2H_5)_2TeI_4$	3.56		1.77	22
$(C_3H_7)_2TeI_2$	3.55	2.25	1.20	22
$(C_3H_7)_2TeI_4$	3.55	2.25	1.19	22
$(C_4H_9)_2TeI_2$	3.53	2.16, 1.50	1.06	25
$(C_4H_9)_2TeI_4$	3.54	2.18, 1.50	1.06	25

[a] Chemical shifts in ppm relative to internal TMS. Uncertainties are ±0.02. Coupling constants in Hz.

Table II. Ultraviolet and Visible Spectra[a]

Compd	Solvent	Peaks (log *E*)	Ref
$(CH_3)_2TeI_2$	Cyclohexane	268 (4.47), 340 (4.27)	2
	Chloroform	272 (4.40), 340 (4.33)	6
$(C_2H_5)_2TeI_2$	Cyclohexane	270 (4.65), 335 (4.36)	2
$(C_3H_7)_2TeI_2$	Chloroform	272 (4.55), 336 (4.30)	*b*
$(C_4H_9)_2TeI_2$	Chloroform	273 (4.58), 335 (4.32)	*b*
$(CH_3)_2TeI_4$	Chloroform	274 (4.49), 336 (4.29), 510 (3.0), 555 sh	2
$(C_2H_5)_2TeI_4$	Cyclohexane	268 (4.75), 335 (4.32), 510 (3.0), 555 sh	2
$(C_3H_7)_2TeI_4$	Chloroform	270 (4.70), 336 (4.40), 510 (3.0)	*b*
I_2	Carbon tetrachloride	512 (2.95)	5
KI_3	Chloroform	292 (nd), 358 (nd), 510 (nd)	*b*
$(CH_3)_4NI_3$	Chloroform	296 (nd), 363 (nd), 511 (nd)	*b*

[a] Peaks in nanometers. nd = not determined; sh = shoulder. [b] This work.

pared ethyl, *n*-propyl, and *n*-butyl analogs.[2,3] These compounds are all covalent solids, black and resembling iodine in general appearance. They form through combination of iodine with dialkyltellurium diiodides in organic solvents.[3] As part of a continuing investigation into the organo derivatives of higher valent tellurium, we studied these compounds in an attempt to determine their structure.

Results and Discussion

Dialkyltellurium tetraiodides dissociate when dissolved in organic solvents. Their solutions show proton nmr spectra (Table I) virtually identical with the corresponding diiodides. The peak patterns are very similar to those of analogous alkyl iodides. No evidence can be found for any diiodide-tetraiodide equilibrium. There is likewise no appreciable difference between the ultraviolet spectra of the diiodides and the tetraiodides (Table II).[4-6] However, the visible spectra do differ; the tetraiodides show a strong peak at 510 nm and a shoulder at 555 nm, while the diiodides show no distinct peaks above 350 nm. There is a marked similarity to the spectra of iodine and triiodides. Addition of I_2 to a solution of Me_2TeI_2 gives a spectrum identical with that of Me_2TeI_4.

Table III shows vibrational peak assignments for Me_2TeI_2, previously reported by Hayward and Hendra,[7] and Me_2TeI_4. The only major difference is a strong band at 160 cm^{-1} in the tetraiodide. Solutions of iodine absorb between 164 and 200 cm^{-1}, depending on solvent,[8] while I_2-R_2S adducts[9] show the I-I stretch at 170 cm^{-1}. The two I-I stretching vibrations in tetramethylammonium triiodide appear at 152 and 111 cm^{-1}, respectively.[10] It seems reasonable, therefore, to assign the 160-cm^{-1} band to the I-I stretch of an I_2 molecule.

Table III. Infrared Spectra

$(CH_3)_2TeI_2$			
Ref 7	This work	$(CH_3)_2TeI_4$	Assignment
	2957		Asym(C-H)
2920 w	2925 m	2905 w	Sym(C-H)
1390 m	Masked	Masked	δ_{asym}(C-H)
1229 w	1228 w	1227 w	δ_{sym}(C-H)
1212 s	1209 w	1212 w	
901, 852 m	902, 848 w	849 w	$\rho(CH_3)$
527 w-m	528 w	518 w	Te-C
190 w-m	188 w	190 w	δ(C-Te-C)
		160 vs, b	I-I
144 s	146 s, b	143 s, b	Asym(Te-I)
113 s	112 m	111 w-m	Sym(Te-I)

Table IV. Major Mass Spectral Peaks

		Rel intens	
m/e	Fragment	$(CH_3)_2TeI_2$	$(CH_3)_2TeI_4$
287	$Me_2{}^{130}TeI^+$	81	28
272	$Me^{130}TeI^+$	43	24
257	$^{130}TeI^+$	28	13
254	I_2^+	100	100
160	$Me_2{}^{130}Te^+$	87	70
145	$Me^{130}Te^+$	85	70
142	MeI^+	87	74
130	$^{130}Te^+$	39	20
127	I^+	78	66

Table IV shows the highest intensity mass spectral peaks for Me_2TeI_2 and Me_2TeI_4. Neither compound shows a molecular ion; in both cases, very weak peaks at *m/e* 384 ($^{130}TeI_2^+$) represent the highest observed values. Both compounds give virtually identical fragmentation patterns. While the *m/e* 254 peak (I_2^+) is strongest in both compounds, it is relatively more intense in the tetraiodide. Noticeably absent is any peak at *m/e* 381, corresponding to I_3^+. Such a peak does appear in the mass spectrum of $Me_4N^+I_3^-$.

There is no evidence that the tellurium atom in R_2TeI_4

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(1) R. H. Vernon, *J. Chem. Soc.*, 119, 687 (1921).

(2) F. L. Gilbert and T. M. Lowry, *J. Chem. Soc.*, 3179 (1928).

(3) J. S. Thayer and K. V. Smith, *Syn. Inorg. Metal-Org. Chem.*, 3, 101 (1973).

(4) T. M. Lowry, R. R. Goldstein, and F. L. Gilbert, *J. Chem. Soc.*, 307 (1928).

(5) E. M. Voigt, *J. Phys. Chem.*, 72, 3300 (1968).

(6) T. M. Lowry and F. L. Gilbert, *J. Chem. Soc.*, 2076 (1929).

(7) G. C. Hayward and P. J. Hendra, *J. Chem. Soc. A*, 1760 (1969).

(8) V. Lorenzelli, *C. R. Acad. Sci.*, 258, 5386 (1964).

(9) M. Yamada, H. Saruyama, and K. Aida, *Spectrochim. Acta, Part A*, 28, 439 (1972).

(10) A. G. Maki and R. Forneris, *Spectrochim. Acta, Part A*, 23, 867 (1967).

has a formal oxidation state of +6. Such oxidizing power as these molecules show comes from iodine. Under vacuum the tetraiodide gives off I_2 vapor to form the diiodide. Dissolving these compounds in olefins and then evaporating also yields the diiodides. Therefore, the formation of dialkyltellurium tetraiodides apparently involves direct incorporation of I_2 molecules, rather than showing iodine-iodine bond cleavage. Dialkyl sulfides and selenides form charge-transfer adducts with iodine,[7,9] while dialkyl tellurides are oxidized to R_2TeI_2.[11] Both α and β forms of $(CH_3)_2TeI_2$ show very extensive Te-I intermolecular interaction in the solid state.[12,13]

In principle, the I_2 molecules could bond to either the Te atom or to an I atom. Infrared and mass spectral studies, however, show no evidence for any triiodide groups in the solid state. Also, the almost negligible change in the Te-I stretching bands going from Me_2TeI_2 to Me_2TeI_4 suggests that the I_2 does not interact to any appreciable extent with the iodine atoms bonded to tellurium. Therefore, the dialkyltellurium tetraiodides most probably are solid-state adducts, perhaps with the distorted octahedral arrangement found for α-Me_2TeI_2 by Chan and Einstein.[12] Such a structure is consistent with the ready dissociation of tetraiodides and also with the observed instability of $(C_4H_9)_2TeI_4$ at room temperature.[3] We could not synthesize either $(C_5H_{11})_2TeI_4$ or $(C_6H_5)_2TeI_4$. The increasing size of the groups would enhance steric effects, hindering I_2 from approaching the tellurium and thereby lowering the stability relative to the diiodide.

Attempts to prepare $(CH_3)_2TeI_2Br_2$ from either the diiodide or the dibromide proved unsuccessful, probably because of the greater electronegativity and reduced size of bromine.

Experimental Section

Both di- and tetraiodides were prepared by methods elsewhere described.[3] Attempted synthesis of $(C_6H_5)_2TeI_4$ or $(CH_3)_2TeI_2Br_2$ by direct combination gave only unreacted starting materials.

Nuclear magnetic resonance spectra were run on a Varian T-60 recording spectrometer, using carbon tetrachloride as solvent and internal tetramethylsilane as standard. Ultraviolet and visible spectra were run on a Cary Model 14 recording spectrophotometer, using 1-cm quartz cells. Peak positions were determined to within ±1 nm. Mass spectra were obtained on a Hitachi Perkin-Elmer RMU-7 mass spectrometer, using an ionizing voltage of 70 eV and a pressure of 2×10^{-6} Torr. Far-infared spectra for the solid compounds were run on a Perkin-Elmer Hitachi FIS 3 spectrophotometer, while the spectra above 400 cm^{-1} were obtained on a Perkin-Elmer Model 337 recording spectrometer. Peak positions were determined to ± 2 cm^{-1}.

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Registry No. $(CH_3)_2TeI_2$, 18879-38-4; $(CH_3)_2TeI_4$, 52585-06-5; $(C_2H_5)_2TeI_2$, 41235-19-2; $(C_2H_5)_2TeI_4$, 52645-35-9; $(C_3H_7)_2TeI_2$, 41235-20-5; $(C_3H_7)_2TeI_4$, 52645-36-0; $(C_4H_9)_2TeI_2$, 41235-21-6; $(C_4H_9)_2TeI_4$, 52730-57-1.

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(11) K. J. Irgolic and R. A. Zingaro, "Organometallic Reactions," Vol. 2, Wiley, New York, N. Y., 1971, pp 117-334.

(12) L. Y. Y. Chan and F. W. B. Einstein, *J. Chem. Soc., Dalton Trans.*, 316 (1972).

(13) F. Einstein, J. Trotter, and C. Williston, *J. Chem. Soc. A*, 2018 (1967).

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Reactions of Dimethyl[diphenyl(*o*-vinylphenyl)phosphine]platinum(II), $Pt(CH_3)_2(SP)$, with Iodine and Iodomethane

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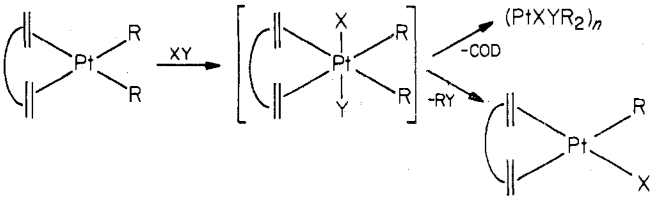
Stable olefin complexes of platinum(IV) are unknown, even for chelating diolefins such as 1,5-cyclooctadiene (COD).[1] Oxidative addition reactions by XY on complexes $PtR_2(COD)$ lead either to polymeric organoplatinum(IV) species, $(PtR_2XY)_n$ not containing COD, or to platinum(II) complexes PtRX(COD), presumably *via* a reactive platinum(IV) intermediate.[1] See Scheme I.

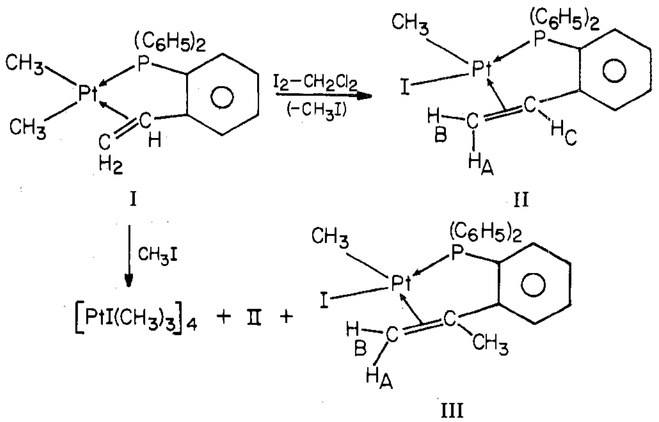
Scheme I



The reaction of $Pt(CH_3)_2(SP)$ (I), where SP = diphenyl(*o*-vinylphenyl)phosphine (*o*-styryldiphenylphosphine), with oxidative-addition reagents promised to be of interest since any platinum(IV)–olefin complex initially formed would be expected to be highly reactive.

The reaction of I with iodine in dichloromethane immediately gave a bright orange solution, suggesting formation of a platinum(IV) species, but the only compound which could be isolated or detected by ^1H nmr was pale yellow $PtI(CH_3)$-(SP) (II), identical in properties with a sample prepared by metathesis from $PtCl(CH_3)(SP)$. Compound II can arise by reductive elimination of iodomethane from a transient intermediate platinum(IV) complex, IVa, which may be monomeric as shown or dimeric with iodide bridges and an uncoordinated vinyl group.

Scheme II



An excess of iodomethane was added to $Pt(CH_3)_2(SP)$ (I) in dichloromethane; the solution was allowed to stand for 2 days and then was evaporated to dryness under reduced

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(1) H. C. Clark and L. E. Manzer, *J. Organometal. Chem.*, 59, 411 (1973).