and is reminiscent of the unusual, rare μ_2-η^1-S_2^{2-} ligand in $(C_5Me_5)_2Cr_2(\mu$-$S_2)_2(\mu$-$S)$.[23] The Fe-Te distances average 2.57 Å and are quite similar to those observed in other $(CO)_x$Fe-Te species.[24,25] The Fe-C and C-O distances in **1** average 1.75 and 1.17 Å, respectively, but little significance can be given to these values.

Spectroscopic Studies

The solution and solid-state IR spectra for the K·crypt salt of **1** are shown in Figure 2. While some minor differences exist between the two spectra, the band frequencies and intensities suggest that the $Fe_2Te_3(CO)_6^{2-}$ ion remains intact in solution. The CO bands for **1** are shifted by ca. 60 cm^{-1} to lower energy relative to those of the parent $Fe(CO)_3(\eta^4$-butadiene) complex.[17] In contrast, the CO bands in the related $M_9Cr(CO)_3^{4-}$ ions (M = Sn, Pb)[3,26] and $M_7Cr(CO)_3^{3-}$ ions (M = As, Sb)[4,27] are red-shifted by 150-200 cm^{-1} relative to the $Cr(CO)_3(\eta^6$-arene) precursors. The trend in CO stretching frequencies among these main-group transition-metal ions is consistent with expectations based on charge per cluster and electronegativities of the main-group atoms.[28]

Conclusion

$Fe(CO)_3(\eta^4$-butadiene) reacts with en extracts of polytellurides in the presence of crypt to form $Fe_2Te_3(CO)_6^{2-}$ (**1**) in good yield. The rate of formation is relatively slow with $t_\infty \approx 18$ h, but **1** is the only carbonyl-containing product present in solution upon completion of reaction even when large excesses of polytellurides are used. The activation of the polytelluride ions by the addition of crypt is directly analogous to the crypt activations of the Sn_9^{4-} and As_7^{3-} ions necessary to form the corresponding $Sn_9Cr(CO)_3^{4-}$ and $As_7Cr(CO)_3^{3-}$ complexes.[3,4] Solution IR spectroscopic studies suggest that **1** maintains its integrity when dissolved. The structure of **1** consists of an $Fe_2(CO)_6$ core with a bridging Te^{2-} ion and an unusual μ_2-η^1-Te_2^{2-} ligand. The Fe-Fe separation is 2.63 (1) Å, which is indicative of an iron-iron single bond. It is interesting to note that **1** and Rauchfuss' $fe_2(\mu$-$Te_2)(CO)_6$ differ only by a single Te^{2-} ion.[28]

Supplementary Material Available: Complete crystallographic summary, ORTEP representations of each $Fe_2Te_3(CO)_6^{2-}$ anion, and complete listings of fractional coordinates, anisotropic thermal parameters, and bond distances and angles (15 pages); a listing of calculated and observed structure factors (58 pages). Ordering information is given on any current masthead page.

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Synthesis and Multinuclear NMR Studies of $[M\{o\text{-}C_6H_4(TeMe)_2\}X_2]$ (M = Pd, Pt; X = Cl, Br, I). The Presence of a Characteristic Ring Contribution to ^{125}Te NMR Chemical Shifts

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The complexes $[M\{o\text{-}C_6H_4(TeMe)_2\}X_2]$ (M = Pd, Pt; X = Cl, Br, I) and $[N^nBu_4][Ir\{o\text{-}C_6H_4(TeMe)_2\}X_4]$ (X = Cl, Br) have been prepared, and characterized by analysis and UV-visible, IR, and multinuclear (^{1}H, ^{195}Pt{^{1}H}, ^{125}Te{^{1}H}) NMR spectroscopy. Two isomers, *meso* and *dl* invertomers, are present in each complex. The coordination shifts in the ^{125}Te NMR spectra of the Pd and Pt complexes are compared with those reported for $[M\{PhTe(CH_2)_3TePh\}X_2]$ and for the analogous *cis*-$[M(TeMePh)_2X_2]$. It is found that, compared with the monodentate complexes, the chelate complexes having five-membered rings exhibit large high frequency coordination shifts and those having six-membered rings have small low frequency shifts. Data on complexes of $o\text{-}C_6H_4(TePh)_2$ and $MeTe(CH_2)_3TeMe$ compared with data for $TePh_2$ and $TeMe_2$ complexes show similar effects, which are rationalized in terms of a characteristic "chelate ring contribution", defined as Δ_R, to the shifts of the bidentate telluroethers. Similar phenomena are known for ^{31}P and ^{77}Se shifts in analogous complexes, but this is the first demonstration of the effect in ^{125}Te NMR.

Introduction

We have recently reported[1] palladium(II) and platinum(II) six-membered chelate ring complexes of two ditelluroethers, $RTe(CH_2)_3TeR$ (R = Me or Ph). Unfortunately $RTe(CH_2)_2TeR$ compounds have not been obtained,[2] but we report here similar complexes of $o\text{-}C_6H_4(TeMe)_2$[3] that contain five-membered chelate rings. In addition to providing a second series of rare chelated ditelluroether complexes,[4] this work allowed the investigation of the effect of ring size upon the ^{125}Te NMR chemical shifts. Many studies of chelating diphosphine complexes[5] have shown that $\delta(^{31}P)$ values are very dependent upon the ring size present. In comparison with the equivalent cis complex containing similar monodentate phosphines, it is observed that five-membered chelate ring diphosphines have large high-frequency coordination shifts, while four- or six-membered rings have small low-frequency shifts. This effect has been systematized in terms of a "chelate ring contribution" to the shifts by Garrou,[6] who also pointed out the usefulness of such an effect in structural assignments. We recently observed similar effects in the ^{77}Se NMR shifts in diselenoether complexes,[7-9] and here we report evidence for the same effect in a third nucleus—^{125}Te.

Experimental Section

Physical measurements were made as described previously.[1] In particular, ^{195}Pt NMR spectra are referenced to external 1 mol dm^{-3} Na_2-

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Table I. Selected Physical Data

complex	color	% C[a]	% H[a]	$\lambda_{max}/10^3$ cm^{-1} (ϵ_{mol}/dm^3 mol^{-1} cm^{-1})[b]	ν(M–X)/cm^{-1} [c]
$[Pd\{o\text{-}C_6H_4(TeMe)_2\}Cl_2]$	yellow	17.8 (16.4)	1.9 (2.0)	25.77 (4800)	295, 284
$[Pd\{o\text{-}C_6H_4(TeMe)_2\}Br_2]$	orange	15.3 (15.1)	1.6 (1.8)	25.00 (2870)	245 (br)
$[Pd\{o\text{-}C_6H_4(TeMe)_2\}I_2]$	dark red	13.3 (13.4)	1.4 (1.5)	22.42 (6190), 30.49 (16660)	
$[Pd\{o\text{-}C_6H_4(TePh)_2\}Cl_2]$	red	32.6 (32.5)	2.1 (2.2)	25.13 (8275), 30.58 (7130) (sh)	298, 274
$[Pt\{o\text{-}C_6H_4(TeMe)_2\}Cl_2]$	yellow	15.3 (15.5)	1.6 (1.7)	31.75 (4360)	329, 306
$[Pt\{o\text{-}C_6H_4(TeMe)_2\}Br_2]$	orange	13.4 (13.7)	1.4 (1.5)	33.56 (9845) (sh)	245 (br)
$[Pt\{o\text{-}C_6H_4(TeMe)_2\}I_2]$	red	11.9 (11.7)	1.2 (1.3)	27.40 (3150)	
$[Ir\{o\text{-}C_6H_4(TeMe)_2\}Cl_4][NBu_4{}^n]$[d]	orange	30.1 (29.8)	4.9 (5.2)		326, 300
$[Ir\{o\text{-}C_6H_4(TeMe)_2\}Br_4][NBu_4{}^n]$[e]	orange	25.8 (25.4)	3.3 (3.4)		280, 254
$[Pd(Me_2Te)_2Cl_2]$	yellow	9.7 (9.7)	2.4 (2.4)	26.18 (31550)	278, 288
$[Pd(Me_2Te)_2Br_2]$	orange	8.3 (8.5)	2.1 (2.2)	25.51 (11750), 32.89 (13430)	260, 278
$[Pd(Me_2Te)_2I_2]$	red	7.1 (7.2)	1.8 (1.8)	22.83 (11680), 29.15 (22090), 35.71 (14470)	
$[Pt(Me_2Te)_2Cl_2]$	pale yellow	8.3 (8.5)	2.1 (2.0)	32.90 (26150), 38.46 (15690)	285, 302, 330
$[Pt(Me_2Te)_2Br_2]$	yellow	7.2 (7.3)	1.8 (1.8)	31.25 (14700), 39.68 (11730)	258, 268
$[Pt(Me_2Te)_2I_2]$	orange	6.3 (6.4)	1.6 (1.6)	28.09 (18340), 36.23 (51950)	
$[Pd(Ph_2Te)_2Cl_2]$	orange	38.9 (39.0)	2.7 (2.7)	24.69 (17550), 29.85 (5616)	280, 285
$[Pd(Ph_2Te)_2Br_2]$	red	34.7 (35.0)	2.4 (2.5)	23.81 (34030), 29.41 (10960)	254, 268
$[Pt(Ph_2Te)_2Cl_2]$	yellow	34.7 (34.8)	2.4 (2.5)	32.26 (23630), 37.04 (54720)	297, 325, 338
$[Pt(Ph_2Te)_2Br_2]$	orange	31.4 (31.3)	2.2 (2.3)	30.30 (18360), 35.46 (34890)	263, 270
$[Pt(Ph_2Te)_2I_2]$	red	28.5 (28.6)	2.0 (2.1)	24.27 (2230), 27.32 (6070), 33.32 (14340)	
$[Pd(PhMeTe)_2Cl_2]$	orange	27.3 (27.3)	2.6 (2.6)	25.32 (27340), 30.30 (12320)	333
$[Pd(PhMeTe)_2Br_2]$	red-brown	23.8 (23.7)	2.2 (2.2)	24.41 (23390), 31.65 (7660)	252
$[Pd(PhMeTe)_2I_2]$	dark brown	21.0 (21.3)	2.0 (2.2)	22.32 (8490), 27.78 (15490), 35.71 (12730)	
$[Pt(PhMeTe)_2Cl_2]$	yellow	23.8 (23.6)	2.3 (2.3)	32.47 (6520), 38.17 (13420)	284, 304
$[Pt(PhMeTe)_2Br_2]$	red	21.2 (21.1)	2.0 (1.9)	30.77 (7420), 38.46 (11860)	234, 251
$[Pt(PhMeTe)_2I_2]$	brown	18.9 (18.7)	1.8 (1.7)	27.52 (6250), 34.48 (12910)	

[a] Calculated (found). [b] In *N,N*-dimethylformamide solution for the bidentates and CH_2Cl_2 solution for the iridium complexes and the monodentates. [c] Nujol mulls. [d] % N: calcd, 1.5; found, 1.5. [e] % N: calcd, 1.3; found, 1.1.

$PtCl_6$ in water and ^{125}Te spectra to neat external Me_2Te, with all shifts reported using the high-frequency positive convention.

Representative Preparations. Dichloro[*o*-phenylene bis(methyl telluride)]platinum(II). The ligand[3] (0.095 g, 0.26 mmol) was added to a rapidly stirred solution of $[Pt(MeCN)_2Cl_2]$ (0.087 g, 0.25 mmol) in dichloromethane (20 cm^3) and the mixture stirred for 4 h. The precipitate that formed was filtered off, rinsed with dichloromethane (5 cm^3) and diethyl ether (20 cm^3), and vacuum-dried. Yield: 0.15 g, 96%. The other $[M(L\text{-}L)X_2]$ (M = Pd, Pt; X = Cl, Br) complexes were made analogously in 80–95% yield.

Diiodo[*o*-phenylene bis(methyl telluride)]palladium(II). Na_2PdCl_4 (0.29 g, 0.99 mmol) was dissolved in ethanol (25 cm^3) and the solution filtered. Sodium iodide (0.6 g, 4 mmol) was added and the solution stirred for 3 h, followed by addition of the ligand (0.36 g, 1 mmol) in ethanol (10 cm^3). The mixture was stirred for a further 1 h, and the precipitate was filtered off, rinsed with diethyl ether (20 cm^3), and dried in vacuo. Yield: 0.54 g, 75%. $[Pt\{o\text{-}C_6H_4(TeMe)_2\}I_2]$ was made analogously. Yield: 80%.

Tetrabutylammonium *cis*-Tetrachloro[*o*-phenylene bis(methyl telluride)]iridate(III), $[N^nBu_4][Ir\{o\text{-}C_6H_4(TeMe)_2\}Cl_4]$. Iridium trichloride hydrate (0.38 g, 1 mmol) and the ligand (0.36 g, 1 mmol) were refluxed together in ethanol (25 cm^3) for 30 min. After the solution was cooled to room temperature, the buff precipitate ($[\{Ir(o\text{-}C_6H_4(TeMe)_2)Cl_3\}_n]$) was filtered off, rinsed with ethanol (100 cm^3), and diethyl ether (10 cm^3) and dried in vacuo. This solid was suspended in 2-methoxyethanol (30 cm^3) containing $N^nBu_4Cl\cdot H_2O$ (1.48 g, 5 mmol), and the mixture was refluxed for 1 h. After cooling, the solution was filtered, the filtrate evaporated under reduced pressure, and the residual oil stirred with ethanol (10 cm^3). An orange solid separated, which was rinsed with ethanol (5 cm^3) and diethyl ether (10 cm^3) and dried in vacuo. Yield: 0.15 g, 15%.

The bromo analogue was made similarly from hydrated iridium bromide in 15% yield.

Dichlorobis(dimethyl telluride)palladium(II). To a rapidly stirred solution of $[Pd(MeCN)_2Cl_2]$ (0.13 g, 0.5 mmol) in acetonitrile (50 cm^3) was added dropwise Me_2Te (0.16 g, 1 mmol), and the mixture was stirred for 1 h. The solution was evaporated to ca. 5 cm^3, and diethyl ether (50 cm^3) was added slowly to precipitate the product. This was filtered off and dried in vacuo. Yield: 0.22 g, 90%. The other monodentate telluride complexes were made analogously in 60–90% yield.

Results and Discussion

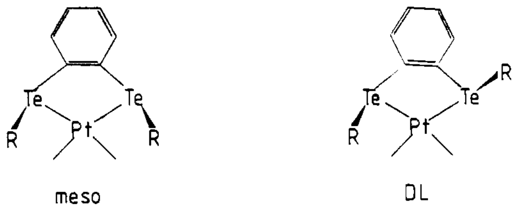

Figure 1. *meso* and *dl* invertomers.

The $[M\{o\text{-}C_6H_4(TeMe)_2\}X_2]$ (M = Pd, Pt; X = Cl, Br) complexes were made in high yield from the ligand and $[M(MeCN)_2X_2]$ in CH_2Cl_2, and the corresponding iodides were prepared from Na_2MCl_4, NaI, and ligand in ethanol. Even with excess ligand, only the 1:1 complexes were formed. Two iridium(III) anions, $[N^nBu_4][Ir\{o\text{-}C_6H_4(TeMe)_2\}X_4]$ (X = Cl, Br) were formed by reaction of $IrX_3{\cdot}nH_2O$ and ligand in ethanol to produce $[\{Ir(o\text{-}C_6H_4(TeMe)_2)X_3\}_n]$ complexes, which were refluxed with excess N^nBu_4X in 2-methoxyethanol to convert them to the anions. The palladium and platinum complexes were very poorly soluble in chlorocarbons, MeCN, or even dimethyl sulfoxide but dissolved fairly well in *N,N*-dimethylformamide (DMF), and this solvent was used for NMR spectroscopic studies. Several complexes of $o\text{-}C_6H_4(TePh)_2$ were made, but these proved to be poorly soluble or decomposed by common solvents, and only one example, $[Pd\{o\text{-}C_6H_4(TePh)_2\}Cl_2]$, was soluble enough for NMR data to be obtained. In contrast the iridium(III) anions were easily soluble even in CH_2Cl_2. The UV–visible and IR spectroscopic data (Table I) are unexceptional but serve to confirm the (cis) planar geometry of the palladium and platinum complexes, and the (cis) octahedral structure of the iridium anions, by comparison with the corresponding data for related complexes.[1,7,10]

NMR Data. **^{1}H.** For [M(ditelluroether)X_2] complexes, two isomers (invertomers) of the coordinated ligand *meso* and *dl* forms (Figure 1) are expected,[1,7,11] and their presence is confirmed by the ^{1}H NMR spectra which show two δ(Me) resonances in each complex, in the cases of the platinum complexes with satellites due to coupling to ^{195}Pt ($I = {}^1/_2$; 33%), with $^3J(^{195}Pt\text{-}^1H) \simeq$ 30–36 Hz. The relative intensities of the two methyl resonances indicate that the two isomers are present in a ca. 1:3 ratio, which varies little with M or X. The ^{125}Te and ^{195}Pt NMR spectra also show

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two resonances in approximate ratio of 1:3, and since the same solvent was used for all the NMR studies, correlation of the resonances in the different spectra by relative intensities was straightforward. For the platinum complexes, the ^{125}Te and ^{195}Pt resonances could be easily correlated via the ^1J coupling constants. The more abundant invertomer, identified as "invertomer 1", had the higher frequency methyl resonance in the proton spectrum of each complex. Previous studies of five-membered-ring dithioethers[11] and diselenoethers[7] have identified the more abundant invertomer as the *dl* form, while in the six-membered rings the *meso* form is more abundant, and *in both cases*, the *meso* invertomer has the higher frequency δ(Me) resonance. This trend also held for $[M(RTe(CH_2)_3TeR)X_2]$ (R = Me, Ph).[1] For the present series of complexes, the ^{1}H NMR data thus suggest that "invertomer 1" is the *meso* form from the relative proton chemical shifts, and if true, the *meso* and not the *dl* form is the more abundant.

^{195}Pt{^{1}H}. Again two resonances are present in the NMR spectrum of each complex, with the more abundant "invertomer 1" resonating at a higher frequency. The difference in the two resonances in each complex was ca. 10–26 ppm, approximately half that found in the six-membered-ring analogues.[1] In the $[Pt\{o\text{-}C_6H_4(TeMe)_2\}X_2]$ complexes, the $\delta(^{195}Pt)$ values shift to low frequency in the order Cl → Br → I, as observed previously[1,7,12,13] with dithioether, diselenoether, and $RTe(CH_2)_3TeR$ complexes, and with the ditelluroethers having the lowest frequency shifts of the three ligand types. Also, consistent with previous observations,[1,12,13,14] the major influences upon the ^{195}Pt chemical shifts are the donor set and the complex geometry (cis/trans), with substituents upon the donors or the chelate ring size having little systematic effect. The absence of marked differences with the chelate ring size contrasts with the effect found in the ^{125}Te NMR data (below).

^{125}Te{^{1}H}. Coordination of $o\text{-}C_6H_4(TeMe)_2$ to a metal results in large high-frequency shifts in the ^{125}Te{^{1}H} resonance, ca. 370–510 ppm, with trans halide dependence $Cl < Br < I$. The trans ligand dependence is the same as that observed in the ^{77}Se NMR of five-membered-ring diselenoethers,[7] but the reverse ordering is found in six-membered rings including $RTe(CH_2)_3TeR$ complexes.[1] A typical spectrum is shown in Figure 2. The coordination shifts are greater for the Pd than for the Pt complexes, with the iridium intermediate, although since the coordination number of the iridium differs this may not be a valid comparison. The spectrum of each complex contains two resonances in the ratio ca. 3:1, with "invertomer 1" having the higher frequency resonance. It is notable that the difference in frequency of the two invertomer resonances is much less ($\leq$20 ppm) than in the six-membered-ring analogues ($\leq$80 ppm).[1] The iodides have the smallest differences, and the resonances in $[Pt\{o\text{-}C_6H_4(TeMe)_2\}I_2]$ are very closely spaced indeed. The invertomer identification by ^{77}Se NMR in diselenoether complexes is that in six-membered rings the *meso* form has the higher frequency resonance, while in five-membered rings the higher frequency belongs to the *dl* form.[7] The ^{125}Te shifts in $[M\{RTe(CH_2)_3TeR\}X_2]$ conform to the same pattern with the *meso* at higher frequency.[1] In $[M\{o\text{-}C_6H_4(TeMe)_2\}X_2]$, the more abundant "invertomer 1" has the higher frequency resonance and thus by comparison with the ^{77}Se NMR data should be the *dl* form. (This conflicts with the ^{1}H data above which suggested "invertomer 1" was the *meso* form.) In the case of six-membered rings with dithioethers,[11] diselenoethers,[7] and ditelluroethers,[1] the relative abundance of the *meso* form increases with donor S < Se < Te.[1] For five-membered rings, data on $MeSCH_2CH_2SMe$, $o\text{-}C_6H_3(Me)(SMe)_2$, $MeSeCH_2CH_2SeMe$, and $o\text{-}C_6H_4(SeMe)_2$ complexes[7,11] show that *dl*:*meso* ratios lie between 2:1 and 1:1, so a reversal of abundance at Te is not unlikely. The identification of "invertomer 1" and "invertomer 2" as *meso* or *dl* is not clear-cut, but overall we feel that "invertomer 1" is probably the *meso*. Hence, even for five-membered ring ditelluroethers, this form is the favored one. The factors that influence the ratio will include ring strain, as a function both of chelate ring size and of donor atom size. Similarly the ^{125}Te (and ^{77}Se) chemical shifts will be affected by the orientation of the free lone pairs, which will also be influenced by the conformational effects of chelation and ring size.

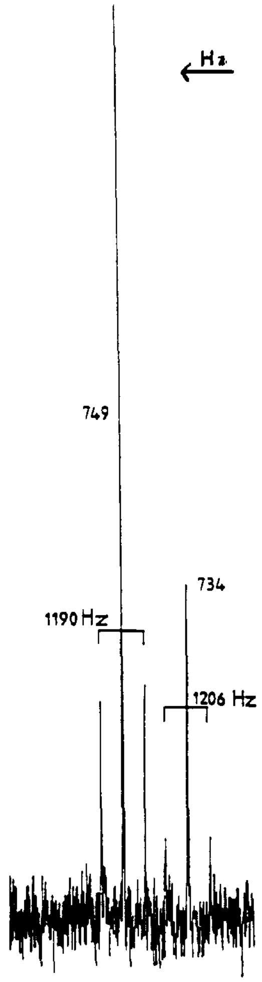

Figure 2. ^{125}Te{^{1}H} NMR spectrum of $[Pt\{o\text{-}C_6H_4(TeMe)_2\}Cl_2]$ in *N,N*-dimethylformamide (140 000 transients).

An X-ray study of a complex has so far been prevented by the poor quality of any crystals obtained, but even if the solid-state structure was determined, it does not follow that this would be of the more abundant invertomer in solution. As we argued elsewhere,[1] when the abundance of the invertomers is significantly different, all examples thus far studied by X-ray crystallography have shown the solid-state structure corresponding to the major solution form. However when the ratios are less disparate, as in the present case, it is not clear that this correlation would hold. There is one example ($[PtMe_3Cl(MeSCH_2CH_2SEt)]$) where the conformation in the crystal was that of the second most abundant invertomer (of four, the relative abundances being 53:23:21:3).[15] The problem could potentially be overcome via an X-ray study combined with a CP/MAS NMR study of the solid and of the mixture of invertomers.[16]

The coupling constants $^1J(^{195}Pt\text{-}^{125}Te)$ decrease with halide in the order Cl > Br > I, reflecting the usual dependence upon the trans influence of the halogens. Similar trends are found in other complexes[1] and in $^1J(^{195}Pt\text{-}^{77}Se)$ in diselenoether analogues.[7,8,11] Little difference in $^3J(^{195}Pt\text{-}^1H)$ couplings were however noted.

The major aim of the present study was to look for a ring contribution to the ^{125}Te NMR shifts, and for this, we required

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Table II. ^1H, $^{125}Te\{^1H\}$, and $^{195}Pt\{^1H\}$ NMR Data for Bidentate Ligand Complexes

	$\delta(^{125}Te)/ppm^{a,b}$		Δ (Te coord)^c		$\delta(^{195}Pt\{^1H\})/ppm^d$		$\delta\{^1H\}/ppm^e$		
compd	isomer 1^f	isomer 2^f	isomer 1^f	isomer 2^f	isomer 1^f	isomer 2^f	isomer 1^f	isomer 2^f	isomer 1/ isomer 2^g
o-$C_6H_4(TeMe)_2$	364								
$[Pd\{o\text{-}C_6H_4(TeMe)_2\}Cl_2]$	851	833	487	469			2.57	2.53	3:1
$[Pd\{o\text{-}C_6H_4(TeMe)_2\}Br_2]$	865	853	501	489			2.63	2.59	3:1
$[Pd\{o\text{-}C_6H_4(TeMe)_2\}I_2]$	871	867	507	503			2.72	2.68	3:1
$[Pt\{o\text{-}C_6H_4(TeMe)_2\}Cl_2]$	749 (1190)	734 (1206)	385	370	−4326	−4336	2.51 (32)	2.48 (32)	3:1
$[Pt\{o\text{-}C_6H_4(TeMe)_2\}Br_2]$	770 (878)	761 (906)	406	397	−4772	−4786	2.57 (34)	2.53 (33)	3:1
$[Pt\{o\text{-}C_6H_4(TeMe)_2\}I_2]$	798 (280)	797 (414)	434	433	−5613	−5639	2.65 (36)	2.61 (34)	3:1
$[Ir\{o\text{-}C_6H_4(TeMe)_2\}Cl_4][N^nBu_4]^h$	779	775	415	411					5:4
$[Ir\{o\text{-}C_6H_4(TeMe)_2\}Br_4][N^nBu_4]^h$	807	800	443	436					4:5
$MeTe(CH_2)_3TeMe$	102								
$[Ir(L\text{-}L)Cl_4][NEt_4]^i$	362.5	357.5	260	255					
$PhTe(CH_2)_3TePh$	456								
$[Ir(L\text{-}L)Cl_4][NEt_4]^i$	541	533	85	76					
o-$C_6H_4(TePh)_2$	692								
$[Pd(L\text{-}L)Cl_2]^j$	896	877	204	185					3:1

^{a}Saturated DMF solution relative to external neat Me_2Te. ^{b} ^1J(Te–Pt) in parentheses (Hz). ^{c}Coordination shift, $\Delta = \delta$(complex) − δ(free ligand). ^{d}Relative to 1 mol dm^{-3} $[PtCl_6]^{2-}$ in H_2O ($\delta = 0$). ^{e}DMF-d_7 solution relative to internal TMS. Methyl resonances only. ^{f}Isomers 1 and 2 are invertomers 1 and 2, respectively. ^{g}Approximate isomer population. ^{h}CH_2Cl_2 solution. ^{i}Data from ref 10. MeCN solution. ^{j}DMSO solution.

Table III. $^{125}Te\{^1H\}$ and $^{195}Pt\{^1H\}$ NMR Data for Monodentate Ligand Complexes

	$\delta(^{125}Te)/ppm\ (^1J(Te\text{-}Pt)/Hz)^a$		Δ (Te coord)^b		$\delta(^{195}Pt)/ppm^c$	
compd	cis	trans	cis	trans	cis	trans
$[Pd(Me_2Te)_2Cl_2]$	248	253	248	253		
$[Pd(Me_2Te)_2Br_2]$	227	239	227	239		
$[Pd(Me_2Te)_2I_2]$	159		159			
$[Pt(Me_2Te)_2Cl_2]$	224 (824)	234 (489)	224	234	−4351	−3769
$[Pt(Me_2Te)_2Br_2]$	215 (540)	220 (342)	216	220	−4733	−4369
$[Pt(Me_2Te)_2I_2]$	172 (80)		172		−5637	
$[Pd(Ph_2Te)_2Cl_2]$	748		63			
$[Pd(Ph_2Te)_2Br_2]$	729		44			
$[Pt(Ph_2Te)_2Cl_2]$	715 (1257)	729 (696)	30	44	−4222	
$[Pt(Ph_2Te)_2Br_2]$	716 (933)	722 (525)	31	37	−4700	−4378
$[Pt(Ph_2Te)_2I_2]$	682 (256)		−3		−5623	
$[Pd(PhMeTe)_2Cl_2]$	487	484	157	154		
$[Pd(PhMeTe)_2Br_2]$	460	458	130	128		
$[Pd(PhMeTe)_2I_2]$	391		61			
$[Pt(PhMeTe)_2Cl_2]$	489 (1356) 489 (1392)	468 (720) 467 (763)	159	138	−4174 −4178	
$[Pt(PhMeTe)_2Br_2]$	471 (824) 470 (...)	455.1 (488) 455 (500)	141	125		
$[Pt(PhMeTe)_2I_2]$	412.4 (232) 411.7 (244)		82		−5629 −5632	

^{a}Saturated CH_2Cl_2 solution relative to external neat Me_2Te. ^{b}Coordination shift (δ(complex) − δ(free ligand)). ^{c}Relative to external 1 mol dm^{-3} $[PtCl_6]^{2-}$ in H_2O ($\delta = 0$).

data on a range of monodentate telluroether complexes.

$[M(TeR_2)_2X_2]$ (R_2 = Me_2, Ph_2, PhMe). A variety of monodentate telluroether complexes of Pd(II) and Pt(II) have been reported, and the incomplete and sometimes contradictory literature has been well reviewed by Gysling.[17] In many cases both cis and trans isomers have been reported, and cis ↔ trans isomerization in solution is solvent-dependent and facile. For our purposes we required ^{125}Te NMR shifts for *cis*-$[M(TeR_2)_2X_2]$, and thus we did not attempt to separate the isomers, nor do we wish to speculate on the solid-state geometries. The only previous data appears to be on $[Pt\{Te(CH_2CH_2Ph)_2\}_2Cl_2]$, which showed that the cis isomer has both a lower frequency ^{125}Te resonance and a larger coupling constant $^1J(^{195}Pt\text{-}^{125}Te)$ than the trans.[18] Our data on complexes of Me_2Te, Ph_2Te, and PhMeTe are shown in Table III, and a typical spectrum is shown in Figure 3. Most complexes showed two isomers present in CH_2Cl_2 solution. Isomer identification for the platinum complexes was made on the grounds of $^1J(^{195}Pt\text{-}^{125}Te)$ being larger for the cis isomer, and from the position of the ^{195}Pt resonances, that of the trans isomer is usually found to substantially high frequency of the cis.[13] The ^{125}Te data was less helpful in that the two resonances were not greatly different (≤20 ppm). For $[Pd(R_2Te)_2X_2]$, it was assumed that the relative cis/trans shifts paralleled those in the platinum analogues. For the TePhMe complexes there is a further complication, in that the coordinated Te center is chiral, and the presence of two such groups leads to *SR*/*RS* and *RR*/*SS* enan-

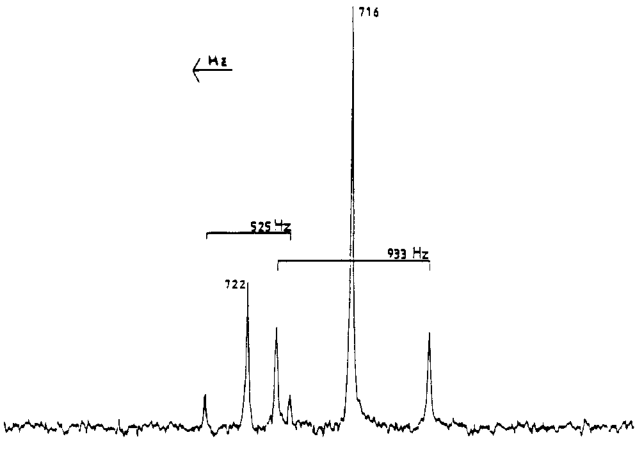

Figure 3. $^{125}Te\{^1H\}$ NMR spectrum of $[Pt(Ph_2Te)_2Br_2]$ in CH_2Cl_2 solution (40000 transients).

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Table IV. Chelate Ring Parameters Δ_R

	Δ_R			
	five-membered ring L–L = *o*-$C_6H_4(TeMe)_2$		six-membered ring L–L = $PhTe(CH_2)_3TePh$[a]	
compd	*meso*	*dl*	*meso*	*dl*
[Pd(L–L)Cl_2]	333	315	–22	–54
[Pd(L–L)Br_2]	373	361	–20	–53
[Pd(L–L)I_2]	446	442	–5	–40
[Pt(L–L)Cl_2]	248	233	–27	–53
[Pt(L–L)Br_2]	281	272	–22	–52
[Pt(L–L)I_2]	351	351	–13	–39
[Pd{*o*-$C_6H_4(TePh)_2$}Cl_2]	148	129		
[Pd{$MeTe(CH_2)_3TeMe$}Cl_2][a]			71	–10
[Pd{$MeTe(CH_2)_3TeMe$}Br_2]			70	–10
[Pd{$MeTe(CH_2)_3TeMe$}I_2]			59	0
[Pt{$MeTe(CH_2)_3TeMe$}Cl_2]			50	–13
[Pt{$MeTe(CH_2)_3TeMe$}Br_2]			41	–12
[Pt{$MeTe(CH_2)_3TeMe$}I_2]			40	1

[a] $\delta(^{125}Te)$ shifts are given in ref 1.

tiomers, which could interconvert by pyramidal inversion at the Te.[19] For the platinum complexes, both cis and trans isomers were found to exhibit a very small splitting (<1 ppm) of the ^{125}Te resonances, which we attribute to these enantiomers, but for the palladium analogues no splittings were resolved, either because they are too small or because the inversion is rapid at room temperature. Further studies of this effect will be reported elsewhere, and for the calculations below, average values were used. In some cases only one geometric isomer was observed, and here the cis/trans assignment is unclear. In practice as we show below this is not a great problem since the differences between cis and trans isomers were small compared with the effect of chelate ring size in the bidentates, and use of the ^{125}Te shift for the trans isomer (in error) in these calculations would not invalidate the calculations.

The Chelate Ring Parameter Δ_R. Following Garrou,[6] we define first the coordination shift Δ as

$$\delta(^{125}\mathrm{Te})_{\mathrm{complex}} - \delta(^{125}\mathrm{Te})_{\mathrm{free\ ligand}} = \Delta$$

and subsequently the chelate ring parameter Δ_R as

$$\Delta_{\mathrm{chelate\ complex}} - \Delta_{\mathrm{equivalent\ cis\ monodentate\ complex}} = \Delta_R$$

The results are shown in Table IV. Ideally, one would compare $RTe(CH_2)_nTeR$ ($n = 2, 3$) compounds but since $RTe(CH_2)_2TeR$ compounds are unknown,[2] Δ_R for the six-membered rings in $PhTe(CH_2)_3TePh$ complexes will be compared with Δ_R for the five-membered rings in those of *o*-$C_6H_4(TeMe)_2$. For complexes of the latter, the "equivalent" monodentate ligand is PhMeTe in *cis*-$[M(TeMePh)_2X_2]$. For $PhTe(CH_2)_3TePh$, the nearest equivalent monodentate would be $PhTe^nPr$ or $PhTe^nBu$ since substituent effects as remote as the γ-carbon can affect ^{125}Te shifts.[2,20] However complexes of neither ligand have been reported, and thus PhMeTe is again used. Similarly one could calculate Δ_R for $MeTe(CH_2)_3TeMe$ complexes using Me_2Te as the monodentate equivalent and for *o*-$C_6H_4(TePh)_2$ complexes using $TePh_2$. For the last two ditelluroethers, there is no structurally equivalent ligand with the other ring size, but the magnitudes of Δ_R are of interest and as will be seen support the arguments presented.

The data (Table IV) clearly show that for five-membered rings Δ_R has a large positive value while for six-membered rings Δ_R is negative for $PhTe(CH_2)_3TePh$ complexes and varies from small positive to small negative values for $MeTe(CH_2)_3TeMe$ complexes. In view of the approximations that are involved, (set out above) great reliance should not be placed upon the actual numerical values, but the trend is clear and unequivocally demonstrates that a chelate ring contribution to ^{125}Te NMR shifts is present in the chelate complexes. The same effects are apparent in the two iridium complexes. The values of the coordination shift Δ for $[Ir(L–L)Cl_4]^-$ are for L–L = $PhTe(CH_2)_3TePh$ (85, 76 ppm) and L–L = *o*-$C_6H_4(TeMe)_2$ (443, 436 ppm) consistent with a Δ_R component that is large and positive for the five-membered ring and small for the six-membered ring, since they would be compared with the *same* monodentate as a model in the unknown[21] *cis*-$[Ir(TePhMe)_2Cl_4]^-$. It would thus seem likely that the chelate ring parameter is a general effect and likely to be present in complexes with any metal. Further data on other metals is clearly required to establish the generality, and data on more closely related "equivalent monodentates" would allow the calculations to be refined. Theoretical explanations of the chelate ring component remain unclear.[5,6]

Conclusion

The presence of a chelate ring contribution to ^{125}Te NMR chemical shifts of chelated ditelluroethers has been demonstrated for the first time. This is the third (after ^{31}P and ^{77}Se) nucleus to show this effect, which promises to be useful in structural assignments in telluroether coordination chemistry.

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