reciprocal field were flat to 1%. Fields were calibrated with standard solutions of nickel chloride and with $HgCo(NCS)_4$.

Results and Discussion

Figure 1 shows as a function of temperature the observed reciprocal molar susceptibility of $Gd_{0.15}WO_3$ and of $Tb_{0.15}WO_3$. In neither case has there been any correction made for diamagnetism of the rare earth ion and the host WO_3 or for the Pauli paramagnetism of the electron gas. As Ostertag has indicated, these corrections almost cancel each other, and, in any case, the observed susceptibilities are so large that either correction would be insignificant. Table I shows the observed magnetic parameters as referred to a Curie–Weiss law $\chi = C/(T - \Theta)$ with the effective magnetic moment $\mu_{\text{eff}} = (3kC/N)^{1/2}$. Calculated moments for comparison are obtained from $\mu = g[J(J + 1)]^{1/2}$ for the ground states of the free ions—*viz.*, $^8S_{7/2}$ for Gd^{3+} ($4f^7$, $g = 2$, $S = 7$, $L = 0$, $J = 7/2$) and $^7F_6$ for Tb^{3+} ($4f^8$, $g = 1.5$, $S = 3$, $L = 3$, $J = 6$). The very small values of the Weiss parameter Θ and the excellent agreement between the observed μ_{eff} and the calculated μ indicate that each of the compounds is magnetically ideal. The agreement observed is about as good as that observed for the magnetically dilute hydrated sulfates (*e.g.*, in $Gd_2(SO_4)_3 \cdot 8H_2O$ the observed μ_{eff} is 7.91 BM and Θ is about 2°; in $Tb_2(SO_4)_3 \cdot 8H_2O$, μ_{eff} is 9.50 BM and $\Theta = 16°$).

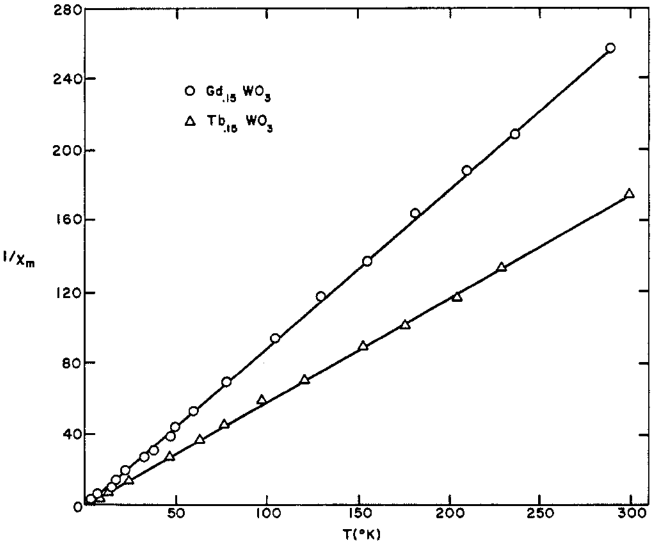

Figure 1.—Reciprocal molar susceptibility *vs.* temperature for gadolinium–tungsten bronze and terbium–tungsten bronze.

TABLE I

MAGNETIC PARAMETERS FOR GADOLINIUM– AND TERBIUM–TUNGSTEN BRONZES

Compn	Θ, °K	μ_{eff}, BM	μ_{calcd}, BM
$Gd_{0.15}WO_3$	2 ± 2	7.90	7.94
$Tb_{0.15}WO_3$	5 ± 2	9.76	9.72

That the rare earth–tungsten bronzes should show such close fit to ideal Curie behavior and that this fit should hold to such very low temperature is not entirely expected. Granted that in $Gd_{0.15}WO_3$ and $Tb_{0.15}WO_3$ the Gd^{3+} and Tb^{3+} are so far apart (7.2 Å, on the average) that direct dipolar interaction is negligible, there still remains the possibility of the Ruderman–Kittel indirect exchange interaction through the conduction electrons.[8] Since the polarization of an itinerant electron changes sign in oscillating manner as the distance from a magnetic atom increases, one would expect moment alignment of neighboring magnetic ions either parallel (ferromagnetic) or antiparallel (antiferromagnetic) depending on the distance from the original magnetic ion.

This kind of analysis, however, is valid only if the conduction electrons use the atomic orbitals of the magnetic ion, so that dipole interaction between the itinerant electrons and the localized moment can occur. If, for example, in Gd_xWO_3, the conduction electrons do *not* use gadolinium orbitals but are confined to the W 5d t_{2g}–O p_π network, then the interaction may be too weak to align the localized moments either parallel or antiparallel. In general, 4f orbitals are too highly localized to contribute appreciably to conduction band states; also, the probability of exciting a 4f electron into a conduction band (5d or 6s) is not very likely.

The fact that Ostertag found a Néel temperature and antiferomagnetic coupling for uranium–tungsten bronze suggests that the case of uranium is different. One possible reason for this is that the uranium magnetic moment comes from 5f orbitals, which have larger spatial extent than 4f and hence may participate in conduction band states; another possibility is that the 5f orbital which carries the magnetic moment is close enough in energy to the 6d to be easily excited to it. In such case the spatial extent of the localized moment would be even greater and interaction with the conduction band more effective.

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CONTRIBUTION FROM RESEARCH AND DEVELOPMENT,
SUN OIL COMPANY, MARCUS HOOK, PENNSYLVANIA 19061,
AND THE DEPARTMENT OF CHEMISTRY, UNIVERSITY OF DELAWARE,
NEWARK, DELAWARE 19711

Far-Infrared Spectra (40–400 Cm^{-1}) of Palladium(II) Isothiocyanate and Isoselenocyanate Complexes Undergoing Linkage Isomerization in the Solid Phase and of Related Complexes

BY JAMES L. LAUER,*[1a] MELVIN E. PETERKIN,[1a] JOHN L. BURMEISTER,[1b] KAREN A. JOHNSON,[1b] AND JOHN C. LIM[1b]

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Linkage isomerization is a process still incompletely understood. A pair of true linkage isomers is difficult to obtain since, in general, one form is much more

(1) (a) Sun Oil Co. (b) University of Delaware.

stable than the other. One instance where the pure isomers could be isolated and where, moreover, the rates of isomerization are easily amenable to study at or near room temperature is the isomerization of [Pd(Et$_4$dien)(SCN/NCS)][B(C$_6$H$_5$)$_4$] (Et$_4$dien = *N*, *N*,*N*′,*N*′-tetraethyldiethylenetriamine), which was described by Burmeister, Gysling, and Lim[2a] and by Burmeister, Hassel, and Phelan.[2b] It occurs S→N bonded in solution and N→S bonded in the solid phase. The corresponding complexes containing Se instead of S were also prepared and found to behave analogously. The principal means for the identification of the bond types was the mid-infrared spectrum: the CN stretching frequencies are generally lower in M–NCS (M = metal atom) complexes than in M–SCN complexes, and the CS stretching frequencies, the NCS bending frequencies, and the corresponding frequencies for Se in place of S all show consistent differences depending on whether the complex is N or S or Se bonded (*cf.* ref 3).

In a continuing study of the mechanism of this isomerization, particularly in the solid phase, identification and observation of the metal–ligand stretching frequencies was considered to be a necessary prerequisite. Intermediates could conceivably be deduced from shifts in the wave number of the corresponding far-infrared absorption peaks and from abrupt changes of the isomerization rates calculated from the corresponding band intensities. Differences between rates calculated from changes of absorption in the Pd–N stretching region and in the CN stretching region can be of considerable help in assessing the mechanism of the isomerization reaction. The recent discovery of Barrer[4] that solid Co(α-CH$_3$py)$_4$(CNS)$_2$ gives a type IV isotherm with xenon, indicating the formation of fresh sites after the uptake of a certain quantity of xenon (*cf.* ref 5), and our own observation that the linkage isomerization rate of our materials in the solid phase may depend on the suspending medium provided further impetus for our work.

The Et$_4$dien ligand and the B(C$_6$H$_5$)$_4$ counterion contribute to complexity and broadness of the far-infrared spectra. Yet, even for simpler complexes, only the assignment of the Pd–S stretching mode for the SCN ligand near 310 cm^{-1} has been agreed on reasonably well in the literature; the Pd–N stretching mode has been assigned to absorption bands lying either 20–40 cm^{-1} above or below 310 cm^{-1} by different authors,[6,7] and no assignments have been made for the corresponding SeCN ligand. Accordingly, this situation had to be clarified.

All samples were synthesized and purified as described elsewhere.[2a] For this study, the samples of the isomerizing materials were examined as Nujol mulls sandwiched between polyethylene plates. Circular washers of about 1-cm i.d. were used as spacers. These sandwiches were kept in an oven at 40° for 2–3 weeks and their far-infrared spectra were obtained nearly every day. An RIIC FS-720 interferometer, covering the 40–400-cm^{-1} region, was used with a theoretical resolution of better than 2.4 cm^{-1}. (The performance of this apparatus has been described in detail by Milward[8] and our modifications of it for small samples and computational procedures can be found elsewhere.[9])

Figures 1 and 2 show, for illustration, the far-infrared spectra of the starting and end material in the series of an –NCS to –SCN isomerization. The corresponding Se spectra are similar. The strongly rising slope of the –NCS trace, attributable to excessive scattering, had to be tolerated so as to be left with an acceptable spectrum for the end material, which contained about 1:3 proportions of N- and S-bonded isomers. By contrast, the corresponding isomerization of the Se compound proceeded faster and went nearly to completion. In both the S and the Se isomerizations the strongest developing absorption band falls at about 320 cm^{-1} and must, therefore, be assigned to the Pd–S or Pd–Se stretching mode. The coincidence of these two modes is not as surprising as it seems: Pluscec and Westland[10] assigned an absorption band at 315 cm^{-1} to both Pd–S and Pd–Se stretching frequencies in "disulfide" and "diselenide," *viz.*, (C$_6$H$_5$)YC$_3$H$_6$Y(C$_6$H$_5$), Y = S or Se, coordinated to a palladium halide, and explained the coincidence in terms of a greater π-bonding ability of Se compared to S, thus compensating for the former's

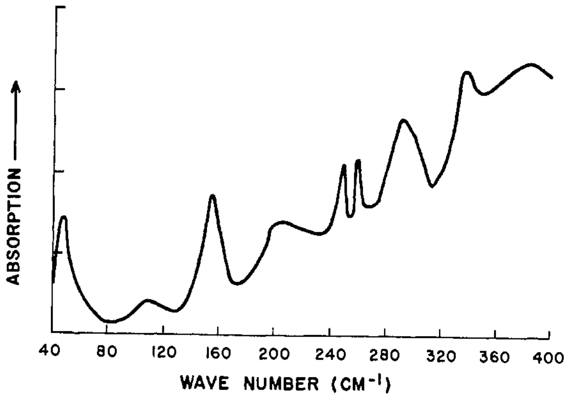

Figure 1.—Far-infrared spectrum of [Pd(Et$_4$dien)NCS][B(C$_6$H$_5$)$_4$], the starting material in the isomerization experiment.

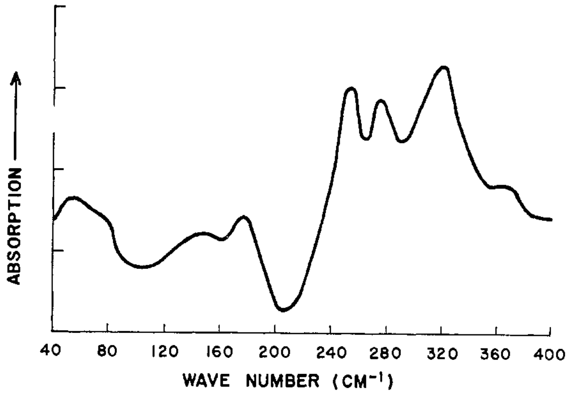

Figure 2.—Far-infared spectrum of [Pd(Et$_4$dien)SCN][B(C$_6$H$_5$)$_4$], the final equilibrium product of isomerization.

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[2] (a) J. L. Burmeister, H. J. Gysling, and J. C. Lim, *J. Amer. Chem. Soc.*, **91**, 66 (1969); (b) J. L. Burmeister, R. L. Hassel, and R. J. Phelan, *Chem. Commun.*, 679 (1970).

[3] P. C. H. Mitchell and R. J. P. Williams, *J. Chem. Soc.*, 1912 (1960).

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[6] D. Forster and D. M. L. Goodgame, *Inorg. Chem.*, **4**, 715 (1965).

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[8] R. C. Milward in "Molecular Spectroscopy," P. Hepple, Ed., Elsevier, Amsterdam, 1968, pp 81–96.

[9] J. L. Lauer and M. E. Peterkin in "Developments in Applied Spectroscopy," Vol. 9, E. L. Grove and A. J. Perkins, Ed., Plenum Press, New York, N. Y., 1971, pp 73–108.

[10] J. Pluscec and A. D. Westland, *J. Chem. Soc.*, 5371 (1965).

greater mass. Burmeister and Lim[11] observed that in solution [Pd(Et$_4$dien)SeCN][B(C$_6$H$_5$)$_4$] isomerized to its N-bonded isomer at a slower rate than that of the corresponding Pd–SCN → Pd–NCS isomerization, indicating stronger bonding of the former. The only band of reasonable strength and location to correspond to the Pd–NCS stretch falls at 365 cm^{-1} in the S and at 360 cm^{-1} in the Se series. Our work, thus, confirms the assignment of Forster and Goodgame[6] (the Pd–N stretching frequency is above the Pd–S stretching frequency). (However, these authors studied similar but not the same complexes.) These assignments were quite clearly developed from the examination of the two series of spectra. From the integrated absorbances about these frequencies first-order reaction rates were calculated for the isomerization processes. The half-lives computed from them are 1.6 days for the Se and 2.2 days for the S complex and these values are similar to those calculated in ref 2a from changes in the 2000–2200-cm^{-1} region.

To substantiate these assignments the far-infrared spectra of the corresponding complexes with the I, Br, Cl, NCO, N$_3$, and NO$_2$ ligands were also obtained, as were those of the SCN and SeCN complexes containing dien (diethylenetriamine) substituted for Et$_4$dien. Table I summarizes the assignments for the metal–ligand stretching modes and shows them to be consistent.

TABLE I

FREQUENCY ASSIGNMENTS

Str modes	Infrared freq, cm^{-1} This work	Infrared freq, cm^{-1} Closest lit.	Ref
Pd–I	168	. . .	. . .
Pd–Br	251	241	12
Pd–Cl	330	333	12
Pd–NCS	365	290–320	7, *a*
Pd–NCSe	360	. . .	. . .
Pd–NCO	365	408, 384, 350	7
Pd–SCN	320	315	10
Pd–SeCN	318	. . .	. . .
Pd–N$_3$	380	. . .	. . .
Pd–NO$_2$	320	330	*a*

[a] M. LePostilloc, *J. Chim. Phys.*, **60**, 1319 (1963).

The assignment of the Pd–I stretching frequency proved difficult because the spectrum of the Et$_4$dien complex contained several broad absorption bands in the expected frequency region. The spectrum of [Pd(dien)I]I was, therefore, run from 40 to 400 cm^{-1}, thereby extending the range accessible to Watt and Klett.[12] Sharp and intense bands were obtained (Figure 3), indeed, unusually sharp for this frequency region. However, only the Raman spectrum (Figure 4), which exhibits an exceedingly intense band at 168 cm^{-1} (coincident with one of the infrared bands), could settle the assignment for us. It was obtained for us by Dr. Robert J. Obremski of Spectra Physics Corp., whose help is hereby acknowledged.

Further work is in progress on the mechanism of linkage isomerizations of NCS → SCN with both Pd and Pt as the metal atom and in the presence of various other ligands and counterions and suspending media. In some of them the behavior of the absorption bands corresponding to the M–N and M–S stretching modes does not parallel that of the CN bands as it does in the instances just described. This work will form the subject of a forthcoming publication.

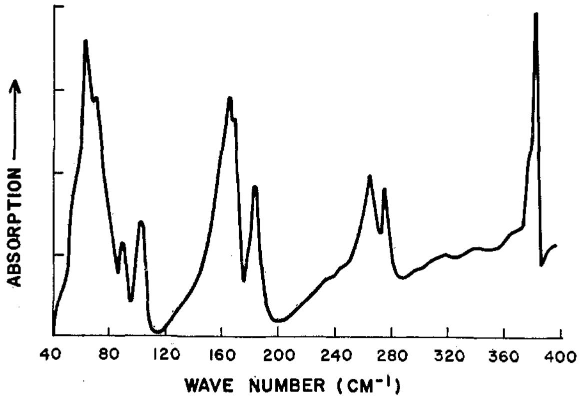

Figure 3.—Far-infrared spectrum of [Pd(dien)I]I.

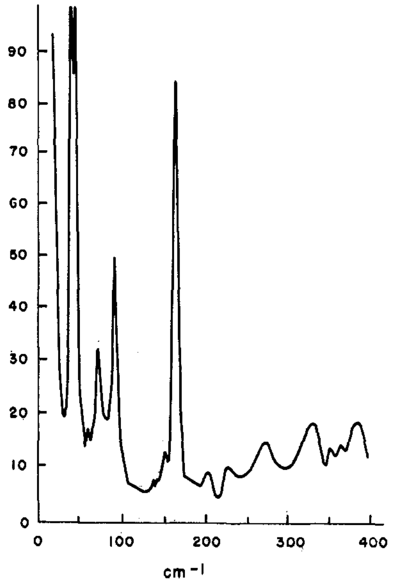

Figure 4.—Raman spectrum of [Pd(dien)I]I.

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CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY,
RUTGERS UNIVERSITY—THE STATE UNIVERSITY, COLLEGE
OF ARTS AND SCIENCES, NEWARK, NEW JERSEY 07102

A Potentiometric Study of Polymeric Anions of Molybdenum in Nitrate Melts

BY JAMES M. SCHLEGEL* AND ROGER BAUER

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There have been conflicting reports in the literature concerning the stable polymeric anions of molybdenum in alkali metal nitrate melts. MoO$_3$ reacts with nitrate

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