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

	Infrared freq, cm^{-1}		
Str modes	This work	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.

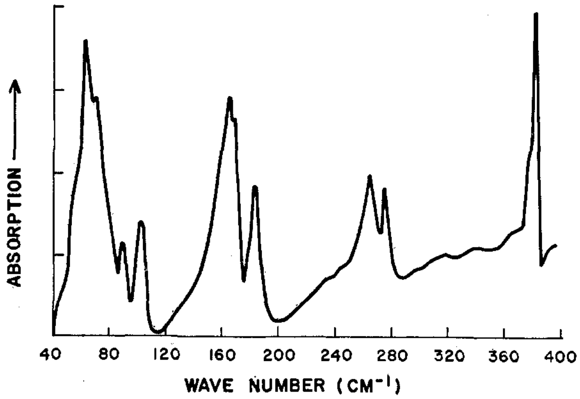

Figure 3.—Far-infrared spectrum of [Pd(dien)I]I.

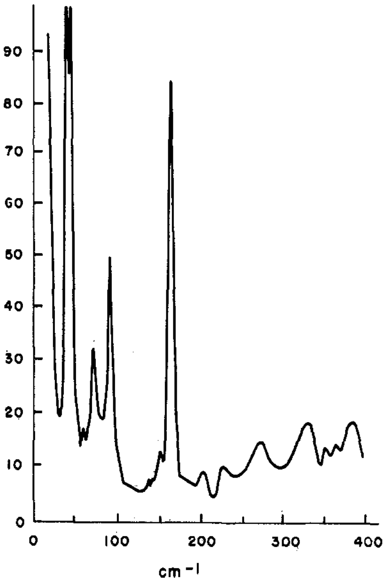

Figure 4.—Raman spectrum of [Pd(dien)I]I.

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[11] J. L. Burmeister and J. C. Lim, *Chem. Commun.*, 1154 (1969).

[12] G. W. Watt and D. S. Klett, *Spectrochim. Acta*, **20**, 1053 (1969).

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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 melts to form oxides of nitrogen and one or possibly more polymeric anions of molybdenum. Shams El Din[1] and coworkers reported that, based upon potentiometric titrations of MoO_3 with Na_2O_2, the species in equilibrium with MoO_4^{2-} is the $Mo_3O_{10}^{2-}$ ion. On the other hand, Kust[2] claimed that $Mo_2O_7^{2-}$ is the stable polymeric anion of molybdenum in equilibrium with MoO_4^{2-}, and he used a galvanic cell to determine the extent of the reaction $2MoO_4^{2-} \rightleftharpoons Mo_2O_7^{2-} + O^{2-}$ in nitrate melts. In addition to repeating the work of Kust and Shams El Din, we tried a different approach to the problem and obtained results which support Kust's conclusion. We offer a possible explanation of why Shams El Din obtained data indicating the trimer to be the stable species.

Experimental Section

Analytical reagent grade chemicals were dried at 150° and stored in a desiccator until needed. Sodium dimolybdate, $Na_2Mo_2O_7$, was prepared by intimately mixing molybdenum(VI) oxide and sodium carbonate in a mole ratio 2:1. This mixture was fused at 850° for 0.5 hr and at 800° for 12 hr, quenched, ground, and stored in a desiccator.

A galvanic cell, previously described,[3] was used to follow oxide ion concentration. Weighed amounts of the reactants were added to 170 g of a nitrate melt and the resulting change in oxide ion concentration was observed potentiometrically. Oxides of nitrogen were carried out of the melt on nitrogen, condensed in a Dry Ice–acetone trap, and then slowly passed through standard base solution. The amount of nitrogen oxides liberated was determined by calculating the amount of base neutralized. Controlled experiments were done to establish the accuracy of this method.

Results and Discussion

We added MoO_3 to a $NaNO_3$–KNO_3 eutectic melt at 330°. The oxide ion concentration was followed with time using our Pt–O_2 electrode, and the liberated nitrogen oxides were collected in a Dry Ice–acetone trap and then analyzed. Contrary to the findings of Shams El Din, our results indicated that $Mo_2O_7^{2-}$ rather than $Mo_3O_{10}^{2-}$ is the polymeric anion in equilibrium with MoO_4^{2-}. Shams El Din's studies were performed at slightly higher temperatures and in pure KNO_3 melts. Therefore, several runs were made at various temperatures and in pure KNO_3 melts to see if the temperature or cation content of the melt determines which polymeric anion predominates. In all cases, for every mole of MoO_3 added to the melt, 1 mol of NO_2 was recovered and 0.5 mol of Na_2CO_3 was required to titrate the remaining acidic species in the melt, Figure 1. These results are consistent with the reaction

$$2MoO_3 + 2NO_3^- \longrightarrow 2NO_2 + 0.5O_2 + Mo_2O_7^{2-} \qquad (1)$$

We then added MoO_4^{2-} to our melt to see what affect it would have on the above reaction and learned that MoO_4^{2-} is a sufficiently stronger base than NO_3^-, such that MoO_4^{2-} can be quantitatively titrated with MoO_3 to yield the dimer $Mo_2O_7^{2-}$

$$MoO_4^{2-} + MoO_3 \rightleftharpoons Mo_2O_7^{2-} \qquad (2)$$

Once the dimer is formed, it can be titrated with Na_2CO_3 back to MoO_4^{2-}

$$Mo_2O_7^{2-} + CO_3^{2-} \rightleftharpoons MoO_4^{2-} + CO_2 \qquad (3)$$

Figure 2 represents typical titration curves that we obtained.

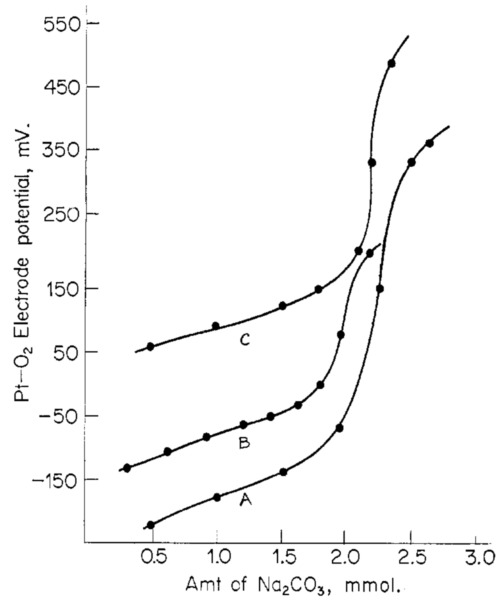

Figure 1.—The titration of the acidic reaction product of MoO_3–NO_3^- melt mixtures (curve A is displaced upward by 50 mV): A, 4.6 mmol of MoO_3 in a $NaNO_3$–KNO_3 eutectic melt at 342°; B, 2.0 mmol of $Na_2Mo_2O_7$ in a $NaNO_3$–KNO_3 eutectic melt at 294°; C, 4.5 mmol of MoO_3 in KNO_3 at 354°.

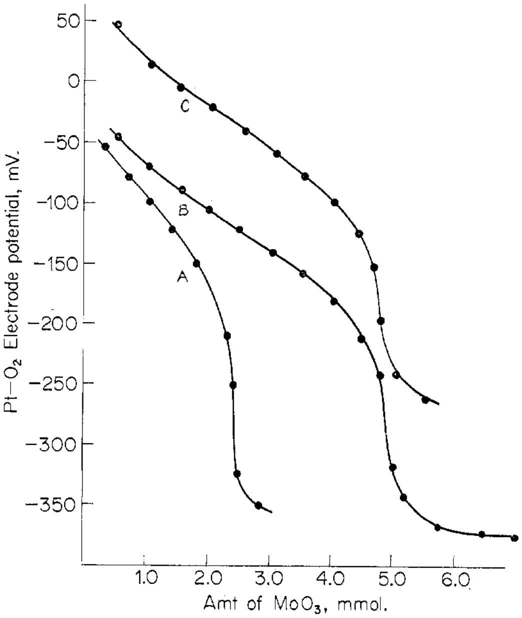

Figure 2.—The titration of MoO_4^{2-} with MoO_3 in nitrate melts: A, 2.5 mmol of MoO_4^{2-} in a $NaNO_3$–KNO_3 eutectic melt at 310°; B, 5.0 mmol of MoO_4^{2-} in a $NaNO_3$–KNO_3 euegcic melt at 338°; C, 5.0 mmol of MoO_4^{2-} in KNO_3 at 348°.

Before the equivalence point, the oxide ion concentration for reaction 3 is determined by the equilibrium reaction $2MoO_4^{2-} \rightleftharpoons Mo_2O_7^{2-} + O^{2-}$. The Pt-$O_2$ electrode responds to oxide ion concentration according to $E = E' + (RT/2F) \ln [O^{2-}]$. Substituting the above equilibrium reaction into this expression and incorporating all constant values including activity coefficients into one term E'', one obtains $E = E'' + RT/2F \ln \{[MoO_4^{2-}]^2/[Mo_2O_7^{2-}]\}$. The concentrations of MoO_4^{2-} and $Mo_2O_7^{2-}$ were determined from the stoichiometry of the reactions. The activity coefficients for MoO_4^{2-} and $Mo_2O_7^{2-}$ are assumed to remain constant since relatively small concentrations of these ions are

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[1] A. M. Shams El Din and A. A. E. Hosary, *J. Electroanal. Chem.*, **9**, 349 (1965).

[2] R. N. Kust, *Inorg. Chem.*, **6**, 2239 (1967).

[3] J. M. Schlegel and R. Bauer, *Chem. Commun.*, 483 (1971).

added to ionic melts. A plot of E *vs.* ln $\{[MoO_4{}^{2-}]^2/[Mo_2O_7{}^{2-}]\}$ should yield a straight line having a slope of $RT/2F$. Several titrations were carried out at various temperatures and concentration ranges. In all cases we obtained a straight line whose slope is in good agreement with the theoretical slope, Figure 3.

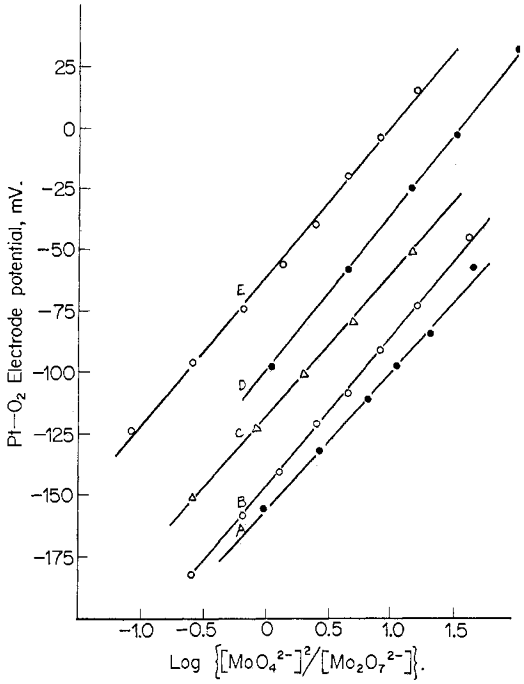

Figure 3.—Nernst plots of a representative sampling of the titrations studied. The points are experimental and the lines are theoretical: A, 2 mmol of $Na_2Mo_2O_7$ in a $NaNO_3$-KNO_3 eutectic melt at 294°; B, 5 mmol of $MoO_4{}^{2-}$ in a $NaNO_3$-KNO_3 eutectic melt at 338°; C, 2.5 mmol of $MoO_4{}^{2-}$ in a $NaNO_3$-KNO_3 eutectic melt at 310°; D, the acidic reaction product of 4.5 mmol of MoO_3 eutectic melt at 354°; E, 5.0 mmol of $MoO_4{}^{2-}$ in KNO_3 at 348°.

There is the possiblility that higher polymers may exist in the nitrate melt; therefore, we continued our titrations of $MoO_4{}^{2-}$ with MoO_3 beyond the first equivalence point to see if a second equivalence point could be obtained. The potential did not change much and NO_2 was slowly produced as more MoO_3 was added to the melt. When MoO_3 is added to pure nitrate melts it is quite evident that MoO_3 is not very soluble and goes into solution as the reaction $2MoO_3 + 2NO_3{}^{2-} \rightarrow 2NO_2 + 0.5O_2 + Mo_2O_7{}^{2-}$ proceeds. However, MoO_3 dissolves rapidly if $MoO_4{}^{2-}$ is present in the melt, even beyond the first equivalence point. This observation indicates that MoO_3 is pulled into solution first by $MoO_4{}^{2-}$ to form the dimer and then by $Mo_2O_7{}^{2-}$ to form the trimer. If the trimer is formed it is too acidic to be stable since NO_2 is generated after the first equivalence point is reached.

To gain further evidence for the dimer, we titrated $Na_2Mo_2O_7$ which we had prepared and found that an equimolar amount of base was required to titrate the $Na_2Mo_2O_7$, Figure 1. A Nernst plot similar to the previous ones gave a straight line within 1% of the theoretical slope, Figure 3.

Finally we duplicated Shams El Din's experiments. That is, we allowed MoO_3 to react with the melt and then titrated the melt with Na_2O_2. We had suspected that the reason our results did not agree with those of Shams El Din was that we had used $CO_3{}^{2-}$ as a base and he had used $O_2{}^{2-}$ as a base. When $CO_3{}^{2-}$ was used as the base, 0.5 mol was required to neutralize the melt for every mole of MoO_3 added. This observation indicated the dimer as the species being formed, eq 1 and 3. When we used $O_2{}^{2-}$ as our base, we obtained inflection points greater than 0.5 mol but less than 0.66 mol of Na_2O_2 added. Two-thirds of a mole would indicate trimer formation, the reaction of MoO_3 with melt being $3MoO_3 + 2NO_3{}^- \rightarrow Mo_3O_{10}{}^{2-} + 2NO_2 + 0.5O_2$ followed by titration with peroxide, $Mo_3O_{10}{}^{2-} + 2O_2{}^{2-} \rightarrow 3MoO_4{}^{2-} + O_2$. Indeed, Shams El Din, who used $O_2{}^{2-}$ exclusively as his base, reported always requiring 0.66 mol of $O_2{}^{2-}$ per mole of MoO_3. We noticed after each titration, however, quantities of unreacted Na_2O_2 in the melt which appeared to be greater than the amount by which we had exceeded the equivalence point. Apparently Na_2O_2 is not very soluble in the melt and is "pulled in" by an acid present in the melt; however, near the equivalence point as the acid concentration becomes more dilute the peroxide will not dissolve readily. Thus, consistently high results are obtained unless one waits long enough for the Na_2O_2 to dissolve and react before taking readings. We found that when we waited sufficiently long on our readings near the equivalence point, very close to 0.5 mol of peroxide was required, thus agreeing with our other data.

There are other properties of peroxide ion which make it an undesirable base titrant. One such property is the tendency for Na_2O_2 to pick up water; therefore appropriate techniques for weighing and transferring accurate quantities are required. Another property, which causes a much more serious problem, is the reaction of peroxide ion with glass in nitrate melts leaving the glass visibly etched. Presumably this effect is more prevalent near the equivalence point of the titration when the acid concentration of the melt is low. Both of these effects will give high results when titrating an acidic species with peroxide ion in nitrate melts.

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A Reinvestigation of the Supposed Linkage Isomerism Exhibited by the *trans*-Dicyanodithiocyanatoaurate(III) Ion

By John B. Melpolder and John L. Burmeister*

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Negoiu and Baloiu recently claimed[1] to have synthesized S- and N-bonded thiocyanate linkage isomers of the title ion, *trans*-$[Au(CN)_2(SCN)_2]^-$, as both the potassium and tetraethylammonium salts. If correct, this would represent the first example of electronic

[1] D. Negoiu and L. M. Baloiu, *Z. Anorg. Allg. Chem.*, **382**, 92 (1971).