and Pt(II) toward inosine and guanosine are mainly due to their difference in ligand-exchange reactions. Thus, Pt(II), being less reactive than Pd(II), reacts slower with the bases. Both metals in aqueous solution first react with the N_7 site of the base and subsequently chelate with O_6. Coordination of Pt at N_7 does not introduce significant geometrical perturbations in the base as was shown[27] in the $[PtCl_3(9\text{-}MeAdeH)]$ complex. In addition, the N_7O_6 distance is suitable for closure of the ring with the metal.

Acknowledgment. We wish to thank Dr. Mantzos of The National Hellenic Research Foundation for the microanalyses and the National Research Council of Canada and the Ministère de l'Education of Quebec for financial assistance.

Registry No. *cis*-$[Pd(InoH)_2Cl_2]$, 64715-03-3; *cis*-$[Pd(Ino)_2]$, 64715-04-4; *trans*-$[Pd(Ino)_2]$, 64753-38-4; *trans*-$[Pd(InoH)_2Cl_2]$, 64753-39-5; $[Pd(InoH)_4]Cl_2$, 64715-05-5; *cis*-$[Pd(InoH)_2(GuoH)_2]Cl_2$, 64715-06-6; *trans*-$[Pd(InoH)_2(GuoH)_2]Cl_2$, 64753-40-8; *cis*-$[Pd(InoH)_2(Cyd)_2]Cl_2$, 64715-07-7; *trans*-$[Pd(InoH)_2(Cyd)_2]Cl_2$, 64753-41-9; *cis*-$[Pd(InoH)_2(XaoH)_2]Cl_2$, 64715-08-8; *trans*-$[Pd(InoH)_2(XaoH)_2]Cl_2$, 64753-42-0; *cis*-$[Pd(H_2O)_2(GuoH)_2]Cl_2$, 63251-58-1; *cis*-$[Pd(GuoH)_2Cl_2]$, 62800-79-7; *trans*-$[Pd(GuoH)_2Cl_2]$, 64753-34-0; *trans*-$[Pd(Guo)_2]$, 64753-35-1; *cis*-$[Pd(Guo)_2]$, 62850-22-0; $[Pd(GuoH)_4]Cl_2$, 64727-96-4; *cis*-$[Pd(GuoH)_2(Cyd)_2]Cl_2$, 64714-96-1; *trans*-$[Pd(GuoH)_2(Cyd)_2]Cl_2$, 64753-36-2; *cis*-$[Pd(GuoH)_2(XaoH)_2]Cl_2$, 64714-97-2; *trans*-$[Pd(GuoH)_2(XaoH)_2]Cl_2$, 64753-37-3; *cis*-$[P(GuoH)_2(Guo)]Cl$, 62800-80-0; $[Pd(GuoH)_3Cl]Cl$, 62800-81-1; *cis*-$[Pd(GuoH)_2(Ino)]Cl$, 64714-98-3; $[Pd(GuoH)_2(InoH)Cl]Cl$, 64714-99-4; *cis*-$[Pd(Cyd)_2Cl_2]$, 64715-00-0; $[Pd(Cyd)_4]Cl_2$, 64715-01-1; *trans*-$[Pd(InoH)_2Tu_2]Cl_2$, 64715-02-2; *trans*-$[Pd(GuoH)_2Tu_2]Cl_2$, 64714-95-0; $K_2[PdCl_4]$, 10025-98-6.

References and Notes

(1) A. T. Tu and M. J. Heller, *Met. Ions Biol. Syst.*, **1**, 1 (1974).
(2) R. Phillips, *Chem. Rev.*, **66**, 501 (1966).
(3) R. M. Izatt, J. J. Christensen, and J. H. Rytting, *Chem. Rev.*, **71**, 439 (1971).
(4) B. Rosenberg, *Platinum Met. Rev.*, **15**, 42 (1971).
(5) N. Hadjiliadis, P. Kourounakis, and T. Theophanides, *Inorg. Chim. Acta*, **7**, 226 (1973).
(6) (a) P. C. Kong and T. Theophanides, *Inorg. Chem.*, **13**, 1167 (1974); (b) *ibid.*, **13**, 1981 (1974).
(7) (a) N. Hadjiliadis and T. Theophanides, *Inorg. Chim. Acta*, **15**, 167 (1975); (b) *ibid.*, **16**, 67 (1976); (c) *ibid.*, **16**, 77 (1976), and references therein.
(8) B. Rosenberg, *Cancer Chemother. Rep., Part 1*, **59**, 589 (1975).
(9) S. Kirschner, A. Maurer, and C. Dragulescu, paper presented at the Third International Symposium on Platinum Coordination Complexes in Cancer Chemotherapy, Oct 18–20, 1976, Dallas, Tex.; *J. Clin. Hematol. Oncol.*, **7**, 190 (1977).
(10) D. J. Nelson, P. L. Yeagle, T. L. Miller, and R. B. Martin, *Bioinorg. Chem.*, **5**, 353 (1976).
(11) (a) M. C. Lim and R. B. Martin, *J. Inorg. Nucl. Chem.*, **38**, 1915 (1976); (b) *ibid.*, **38**, 1911 (1976).
(12) (a) A. A. Grinberg, V. S. Varshavskii, M. I. Gel'fman, N. V. Kiseleva, and D. B. Smolenskaya, *Russ. J. Inorg. Chem.* (*Engl. Trans.*), **13**, 422 (1968); (b) M. I. Gel'fman and N. A. Kustova, *ibid.*, **14**, 10 (1969).
(13) H. I. Heitner and S. J. Lippard, *Inorg. Chem.*, **13**, 815 (1974).
(14) (a) J. P. Maquet and T. Theophanides, *Biopolymers*, **14**, 781 (1975); (b) J. P. Maquet and T. Theophanides, *Bioinorg. Chem.*, **5**, 59 (1975); (c) M. M. Millard, J. P. Maquet, and T. Theophanides, *Biochim. Biophys. Acta*, **402**, 166 (1975).
(15) B. Rosenberg, paper presented at the Third International Symposium on Platinum Coordination Complexes in Cancer Chemotherapy, Oct 18–20, 1976, Dallas, Tex.; *J. Clin. Hematol. Oncol.*, **7**, 817 (1977).
(16) (a) E. Sletten, *J. Chem. Soc., Chem. Commun.*, 558 (1971); (b) E. Sletten, *Acta Crystallogr., Sect. B*, **30**, 1961 (1974).
(17) C. F. Neumann, B. Prijs, and H. Sigel, *Eur. J. Biochem.*, **41**, 209 (1974).
(18) A. D. Kelman, H. J. Peresie, and P. J. Stone, paper presented at the Third International Symposium on Platinum Coordination Complexes in Cancer Chemotherapy, Oct 18–20, 1976, Dallas, Tex.; *J. Clin. Hematol. Oncol.*, **7**, 440 (1977).
(19) S. Mansy, G. Y. H. Chu, and R. S. Tobias, paper presented at the Third International Symposium on Platinum Coordination Complexes in Cancer Chemotherapy, Oct 18–20, 1976, Dallas, Tex.
(20) M. Ogawa and T. Sakaguchi, *Chem. Pharm. Bull.*, **19**, 1650 (1971).
(21) (a) A. T. Tu and J. A. Reinosa, *Biochemistry*, **5**, 3375 (1966); (b) A. T. Tu and C. G. Friedrich, *ibid.*, **7**, 4367 (1968).
(22) N. A. Berger and G. L. Eichhorn, *J. Am. Chem. Soc.*, **93**, 7062 (1971).
(23) J. Dehand and J. Jordanov, *J. Chem. Soc., Chem. Commun.*, 598 (1976).
(24) *cis*-$[Pt(InoH)_2Cl_2]$ in water without NaCl was undergoing the following reaction:[7c] *cis*-$[Pt(InoH)_2Cl_2] \rightarrow$ *cis*-$[Pt(Ino)(InoH)Cl]$ + HCl. This was indicated from (a) HCl liberation (pH decrease), (b) the increase of the conductivity of the solution, due to HCl liberation, and (c) the isolation of the complex $[Pt(Ino)(InoH)Cl]$.
(25) J. M. Gulland and T. F. Macrae, *J. Chem. Soc.*, 2331 (1932).
(26) (a) F. P. Dwyer and D. P. Mellor, "Chelating Agents and Metal Chelates", Academic Press, New York and London, 1964; (b) G. J. Palenik, *Acta Crystallogr.*, **17**, 687 (1964).
(27) (a) A. .Terzis, N. Hadjiliadis, R. Rivest, and T. Theophanides, *Inorg. Chim. Acta*, **12**, L5 (1975); (b) A. Terzis, *Inorg. Chem.*, **15**, 793 (1976).

Contribution No. 3079 from the Department of Chemistry,
Indiana University, Bloomington, Indiana 47401

Reactions of $MoO(S_2CNR_1R_2)_2$ with Azide

E. A. MAATTA and R. A. D. WENTWORTH*

Received May 2, 1977

When an alkylammonium salt of N_3^- is partitioned between water and $CHCl_3$ containing $MoO(S_2CNEt_2)_2$, the slow formation of N_2, NH_3, and $MoO_2(S_2CNEt_2)_2$ occurs. Significant enhancement of the rate of evolution of N_2 occurs when the aqueous layer is acidified and the reaction no longer requires the alkylammonium cation. There are no indications that significant quantities of a protonated Mo(IV) complex occur under the experimental conditions. The results are interpreted in terms of the reaction between HN_3 and $MoO(S_2CNEt_2)_2$ with the formation of a nitrene and N_2. Subsequent hydrolysis of the nitrene produces NH_4^+ and the Mo(VI) complex. Variation of the organic substituents of the dithiocarbamate ligand produces changes in $\nu(C\overset{\cdots}{-}N)$ and $\nu(MoO)$ and decreases in the rate of evolution of N_2 as the complexity of these substituents is increased. An explanation in terms of electronic effects rather than steric hindrance is offered. The decrease in the rate of the reaction of $Mo_2O_3(S_2CNEt_2)_4$ when compared to that of $MoO(S_2CNEt_2)_2$ is rationalized in terms of the disproportionation of the dinuclear complex prior to the reaction with HN_3. The possible biological significance of these reactions as they pertain to the functioning of the nitrogenases is discussed.

Introduction

The dialkyldithiocarbamate complexes of oxomolybdenum(IV), $MoO(S_2CNR_1R_2)_2$, and particularly the derivative with $R_1 = R_2 = C_2H_5$ (Et), have received considerable attention because they are possible models for molybdoenzymes.[1-5] While their reactions with certain activated molecules appear to be reasonably fast in certain instances,[2] reactions with real biological substrates tend to be very slow or even nonexistent under the experimental conditions which have been described. Neither N_2, N_3^-, nor N_2O,[1,5] all of which are substrates for nitrogenases,[6] bind to $MoO(S_2CNEt_2)_2$ or react with it in anhydrous $CHCl_3$. The possibility that this

0020-1669/78/1317-0922$01.00/0

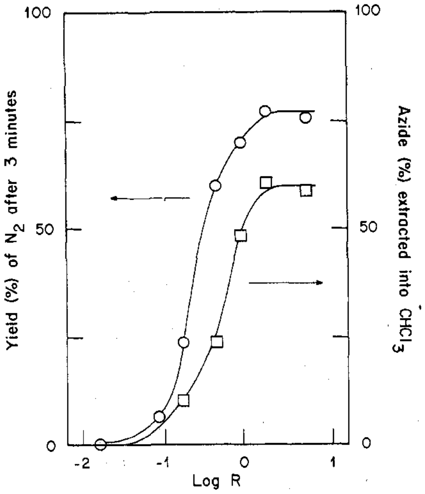


Figure 1. The circles indicate the yield of N_2 after 3 min which results from the reaction of $MoO(S_2CNEt_2)_2$ with azide as a function of log R where $R = [HCl]_0/[NaN_3]_0$. The squares indicate the quantity of azide which is extracted into the organic phase in the absence of $MoO(S_2CNEt_2)_2$ as a function of log R. Further experimental conditions are given in the text.

complex is in any way a legitimate model for nitrogenases would appear somewhat remote unless activation of either the complex or one of the substrates can be achieved. We now wish to report that significant enhancement in the rate of reduction of azide can be obtained by very simple means.

Results and Discussion

Stimulation of the Reaction. When a solution of $MoO(S_2CNEt_2)_2$ and $[(n\text{-}C_3H_7)_4N]N_3$ in $CHCl_3$ is covered by water, slow but eventually quantitative formation of N_2 (1.00 ± 0.05 mol/mol of complex) and NH_3 (0.99 ± 0.02 mol/mol of complex) occurs. These products are identical with those obtained from the biological systems.[6] The slow rate of this process makes it clear that N_3^- is not an efficient oxidant for this complex. A rapid quantitative evolution of N_2 occurs, however, when water is replaced by aqueous HCl (1 M). An indication of the rate can be obtained by measuring the yield of N_2 after a short, fixed time period providing that the time is less than that required for a complete reaction. Identical yields of N_2, and hence identical rates, occur using either NaN_3 or the alkylammonium salt in either 0.25 or 1 M HCl. The effect of the concentration of HCl in the aqueous phase when that phase contains NaN_3 is shown in Figure 1. The conditions for these experiments are $[MoO(S_2CNEt_2)_2]_0 = 0.049$ M in $CHCl_3$ (25 mL), $[NaN_3]_0 = 0.61$ M in aqueous HCl (10 mL), and a fixed stirring rate with a time period of 3 min.[7] No measurable evolution of N_2 occurs within that time span at the lowest acidity (10^{-2} M), but the yield increases as the acidity is increased until a plateau is attained. All of the azide has been converted to HN_3 at this plateau since HN_3 is a weak acid ($pK_a = 4.6$) and log $R > 0$, where $R = [HCl]_0/[NaN_3]_0$. The same figure also contains the results from extracting 10 mL of aqueous NaN_3 (0.61 M) at various concentrations of HCl with 25 mL of $CHCl_3$. Virtually no azide appears in the organic phase at the lowest acidity but a plateau is also attained when log $R > 0$ in accord with the extraction of HN_3 and a distribution ratio, $D = [HN_3]_{org}/[HN_3]_{aq}$, of approximately 0.6. These results show unambiguously that HN_3 is a more efficient oxidant of this Mo(IV) complex than N_3^-, whether that ion is in the aqueous or organic phases.

Limited studies in DMF solutions containing water or aqueous HCl have indicated that a similar situation prevails. When 6.13 mmol of NaN_3 is added to a solution containing DMF (23 mL) and H_2O (2 mL) with $[MoO(S_2CNEt_2)_2]_0 = 0.049$ M, the yield of N_2 after 3 min is only 2%. However, when water is replaced by 6 M aqueous HCl (2 mL), the yield increases to 54% after the same period of time.

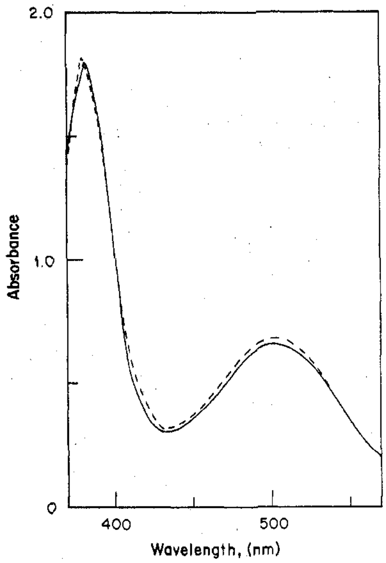


Figure 2. Electronic spectrum of $MoO(S_2CNEt_2)_2$ (9.88×10^{-4} M) in anhydrous $CHCl_3$ (—) and the spectrum of the same solution after equilibration with an aqueous layer (- - -).

Nature of the Mo(IV) and Mo(VI) Complexes. The crystal structure of $MoO(S_2CN(n\text{-}Pr)_2)_2$ has shown that the molecular structure consists of a mononuclear, rectangular-based pyramid with an apical oxygen atom.[8] The mass spectrum of $MoO(S_2CNEt_2)_2$ is also consistent with a mononuclear complex. The molecular weight of $MoO(S_2CN(i\text{-}Pr)_2)_2$, which has been determined in $CHCl_3$ at −30 °C by an isopiestic method[9] in conjunction with some NMR studies, indicates again that a mononuclear complex is present (calcd, 464; found, 465 ± 5). Furthermore, the results obtained from the NMR studies, which will be presented elsewhere, are consistent with a mononuclear, rectangular-based pyramid. Although this structure will permit two isomers when $R_1 \neq R_2$, the infrared spectrum of $MoO(S_2CN(Me)(Bz))_2$ contains only a single absorption which can be assigned to the MoO stretching frequency. If both isomers are present, it is clear that this feature in the infrared spectrum will not serve to distinguish them.

There are two effects which might arise from the aqueous layer and change these conclusions. The first, binding of water at the sixth site of this structure, could produce a complex which is similar to that found[10] for *trans*-$MoO(OH_2)(CN)_4^{2-}$. Small perturbations which are observed in the electronic spectrum of $MoO(S_2CNEt_2)_2$ in anhydrous and wet $CHCl_3$ (Figure 2) might be attributed either to water binding at that site or more probably to subtle effects induced by changes in the structure of the solvent. However, even if expansion of the coordination number of the molybdenum atom does occur, no obvious changes in the reaction with HN_3 would be observed. The second possible effect is a specific interaction with acid causing protonation of the terminal oxygen atom and formation of $Mo(OH)Cl(S_2CNEt_2)_2$. This complex is clearly the probable intermediate in the formation of $MoCl_2(S_2CNEt_2)_2$ from $MoO(S_2CNEt_2)_2$ and dry HCl in benzene,[11] as shown in eq 1. Since $MoCl_2(S_2CNEt_2)$ is green, it can be

$$MoO(S_2CNEt)_2 \underset{}{\overset{HCl}{\rightleftharpoons}} Mo(OH)Cl(S_2CNEt_2)_2 \overset{HCl}{\rightleftharpoons} MoCl_2(S_2CNEt)_2 + H_2O \qquad (1)$$

readily distinguished from the starting material but the color of the intermediate is unknown. If the intermediate is formed under the conditions which were responsible for the data in Figure 1, the results require that the formation of this complex is complete when log $R > 0$ since a constant rate would not otherwise be attained under those conditions. Three pieces of evidence rule out the formation of $Mo(OH)Cl(S_2CNEt_2)_2$ as a major contributing factor, however. When 0.049 M $MoO(S_2CNEt_2)$ in $CHCl_3$ (25 mL) is equilibrated with 0.25 M HCl (10 mL) in the absence of azide, but corresponding to log $R = -0.39$ in Figure 1 if azide were present, titration of the aqueous layer after the organic phase is removed indicates no measurable decrease in the concentration of the acid. Second, when 0.25 M HCl is replaced by either 0.25 M $HClO_4$ or 0.25 M HBF_4 in the presence of 0.61 M NaN_3, the yields of N_2 after 3 min are 59 and 60%, respectively. These results are identical within experimental error to the value of 60% obtained with 0.25 M HCl. Finally, when $MoCl_2(S_2CNEt_2)_2$ in $CHCl_3$ is equilibrated with 1 M HCl, which would correspond to log $R = 0.21$ if azide were present, the organic layer remains green while it is red if $MoO(S_2CNEt_2)_2$ is used at an identical concentration. The differences in color indicate that different complexes are present in solution under the same experimental conditions. Consequently, the reaction shown in eq 1 is not readily reversible under these conditions although the presence of water suggests that it might be. The conclusion is that $MoO(S_2CNEt_2)_2$ (or possibly $MoO(OH_2)(S_2CNEt_2)_2$) is the species which is present for all values of log R in Figure 1.

The nature of the oxidation product containing molybdenum has been determined by infrared spectroscopy. When the initial acidity is low, the product is $MoO_2(S_2CNEt_2)_2$. The product at higher acidities is $MoOCl_2(S_2CNEt_2)_2$, a compound which was obtained previously from the reaction of Cl_2 with $MoO(S_2CNEt_2)_2$ in anhydrous benzene[11] and the addition of concentrated aqueous HCl to a solution of $MoO(S_2CNEt_2)_2$ in acetone.[12]

The results are consistent with the scheme represented by eq 2, 3, 4, and 5. Included in the sequence of reactions is the

$$MoO(S_2CNEt_2)_2 + HN_3 \rightarrow MoO(NH)(S_2CNEt_2)_2 + N_2 \quad (2)$$

$$MoO(NH)(S_2CNEt_2)_2 + H_3O^+ \rightarrow MoO_2(S_2CNEt_2)_2 + NH_4^+ \quad (3)$$

$$MoO(S_2CNEt_2)_2 + MoO_2(S_2CNEt_2)_2 \rightleftharpoons Mo_2O_3(S_2CNEt_2)_4 \quad (4)$$

$$MoO_2(S_2CNEt_2)_2 + 2H_3O^+ + 2Cl^- \rightleftharpoons MoOCl_2(S_2CNEt_2)_2 + 3H_2O \quad (5)$$

inevitable reaction of $MoO(S_2CNEt_2)_2$ with $MoO_2(S_2CNEt_2)_2$ to give $Mo_2O_3(S_2CNEt_2)_4$.[3] This reaction, which should become increasingly important as the oxidation of the Mo(IV) complex progresses, will tend to decrease the concentration of free $MoO(S_2CNEt_2)_2$ which is available for oxidation. However, the $Mo_2O_3(S_2CNEt_2)_4$ that is produced should provide a continuous source of the Mo(IV) complex throughout the course of the reaction. Additional evidence can be found in another section of this paper. Although not shown in these equations, a trans-to-cis isomerization must also occur somewhere within the sequence of reactions. Abstraction of NH from HN_3 to form a nitrene is proposed as the key step in reaction 2. It is noteworthy that abstraction of an oxygen atom, which is isoelectronic with NH, has been postulated as an important step in the mechanisms of the reactions of those oxidases and reductases which contain molybdenum.[2,13]

If HN_3 was immediately available to $MoO(S_2CNEt_2)_2$ upon demand, then either the formation of the nitrene or the formation of a complex with HN_3 which must precede the nitrene would probably be the rate-determining step. The yields of N_2, under these conditions, would tend to parallel the extraction of HN_3 into the organic phase with increasing values of log R. However, the results in Figure 1 indicate that yields of N_2 increase more markedly than the extraction of HN_3. If stirring is replaced by shaking, marked increases in the yields of N_2 after 3 min are found. Consequently, the transfer of HN_3 across the phase boundary, as that reagent is consumed in the organic phase, occurs at rates which are comparable to that of the chemical reaction when the mixture is stirred. Simple kinetics would not be expected under these conditions since the rate equation must account for both reactions. A thorough study would require controlled variation of the stirring rate. Such studies, which are common in phase-transfer catalysis, are not contemplated at present for this reaction.

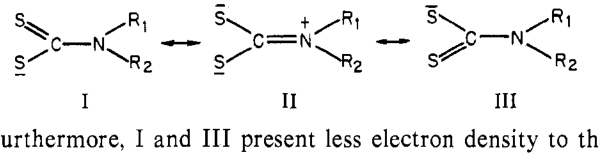
Table I. Yields of N_2 after 3 min upon Oxidation of $MoO(S_2CNR_1R_2)_2$ with Azide in 1 M HCl (log $R = 0.21$) and Infrared Data

R_1	R_2	Yield, %	$\nu(C\overset{\cdots}{-}N)$, cm^{-1}	ν(MoO), cm^{-1}
CH_3	CH_3	98[a]	1550	951
CH_3	$C_6H_5CH_2$	79	1530	961
C_2H_5	C_2H_5	75	1518	962
i-C_3H_7	i-C_3H_7	64	1499	967

[a] This result is even more remarkable since $MoO(S_2CNMe_2)_2$ is only partially soluble in $CHCl_3$.

Although quantitative yields of N_2 are obtained eventually in all cases, the rate of evolution is also somewhat dependent upon the nature of the organic groups which are attached to the ligand as shown in Table I. The nature of these groups influences both the $N\overset{\cdots}{-}C$ and MoO stretching frequencies. Although the rate decreases with increasing bulkiness of R_1 and R_2, it seems unlikely that steric hindrance plays an important role. Molecular models show that ingress by HN_3 to the molybdenum atom should not be impeded by R_1 and R_2 since those groups are considerably removed from the metal atom. Consequently, a rationalization based on electronic effects seem to be required. The effect on the rate due to transfer of HN_3 into the organic phase is ignored in the following discussion and it is assumed that the rate-determining step of the chemical reaction is the binding of HN_3 to the complex.

The decreasing values of $\nu(C\overset{\cdots}{-}N)$ which occur with $R_1 = R_2 = CH_3$, C_2H_5, and i-C_3H_7 are found commonly. This trend was apparently first observed with the Cu(II) complexes[14] and later with others such as the Fe(III) and Fe(IV) complexes[15] as well as the vanadyl complexes.[16] The latter are probably isostructural with their Mo(IV) counterparts. A similar trend seems to exist for the sodium salts of the ligands as well as the Mo(VI) complexes, $MoO_2(S_2CNR_1R_2)_2$, although the data do not contain results with $R_1 = R_2 = i$-C_3H_7.[17] In terms of the resonance structures for the ligand which are shown below, II must become increasingly less important than I or III.



I II III

Furthermore, I and III present less electron density to the metal. As electron density from the ligand is withdrawn, π donation from the terminal oxygen atom may increase which accounts for the increases in ν(MO) which are observed both in the vanadyl complexes[16] and in these Mo(IV) complexes. Couched in a different way, if the d_{xy} and d_{yz} orbitals act as π-acceptor orbitals for both axial bonding to the oxygen atom and equatorial bonding to the sulfur atoms, a decrease in the importance of II will decrease the importance of sulfur-to-metal π bonding and increase the importance of oxygen-to-metal π bonding. It is well-known that the strength of the multiple bond between vanadium and oxygen in vanadyl complexes is responsible for either relatively long bonds from vanadium to ligands bound opposite to the oxygen atom or a vacant site at that position. As the strength of the multiple bond between molybdenum and oxygen increases in the Mo(IV) complexes, it follows that the coordination of HN_3 prior to loss of N_2 should become increasingly more difficult.

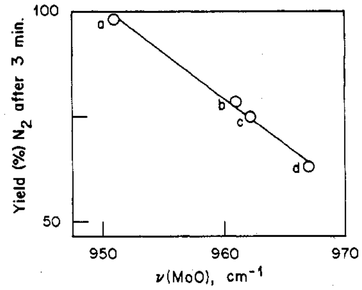


Figure 3. The linear relationship between the yields of N_2 after 3 min from the reactions between $MoO(S_2CNR_1R_2)_2$ and azide and the MoO stretching frequencies for those compounds. The data were obtained for (a) $R_1 = R_2 = CH_3$, (b) $R_1 = CH_3$, $R_2 = C_6H_5CH_2$, (c) $R_1 = R_2 = C_2H_5$, and (d) $R_1 = R_2 = i\text{-}C_3H_7$.

Larger activation energies for the reaction in eq 2 will then result. It is of interest to note that there is a linear relationship between the yields of N_2 after 3 min and ν(MoO) as shown in Figure 3, which again points to the importance of electronic effects.

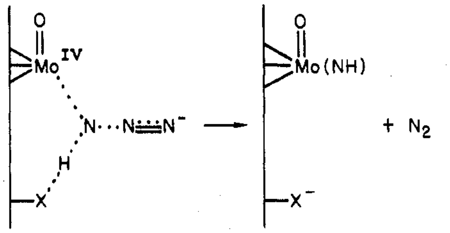
Reactions of $Mo_2O_3(S_2CNEt_2)_4$ with Azide. The dinuclear Mo(V) complex, $Mo_2O_3(S_2CNEt_2)_4$, disproportionates according to eq 6 which is eq 4 reversed. The magnitude of the

$$Mo_2O_3(S_2CNEt_2)_4 \rightleftarrows MoO(S_2CNEt_2)_2 + MoO_2(S_2CNEt_2)_2 \qquad (6)$$

equilibrium constant for this reaction, which is approximately 10^{-3} at 41 °C in chlorobenzene,[18] is not known when the solvent is $CHCl_3$. However, it is sufficiently large to cause a marked deviation from the Beer–Lambert law.[3]

The conditions for the reactions of this complex with azide are identical with those employed with the Mo(IV) complexes but at an initial aqueous acidity provided by 1 M HCl (log R = 0.21) and $[Mo_2O_3(S_2CNEt_2)_2]_0 = 0.050$ M in $CHCl_3$. The yield of N_2 after 3 min is 51%. A quantitative yield corresponding to the two-electron oxidation of the dinuclear complex requires a somewhat longer time. When the same reaction is conducted using a saturated solution of $MoO_2(S_2CNEt_2)_2$ in $CHCl_3$, where the approximate concentration of that reagent is 0.25 M, the yield of N_2 after 3 min drops to 34%. As shown in Table I, the reaction between $MoO(S_2CNEt_2)_2$ and azide under the same conditions affords a 75% yield of N_2 after the same period of time. These results are consistent with the assumption that a major portion of the reaction using the dinuclear complex proceeds by a path which involves disproportionation followed by the reaction of $MoO(S_2CNEt_2)_2$ with HN_3. Since the disproportionation of $Mo_2O_3(S_2CNEt_2)_4$ is fast,[19] and undoubtedly more rapid than the reaction of $MoO(S_2CNEt_2)_2$ with HN_3, the rate constant for the initial reaction should be directly proportional to the product of the equilibrium constant for disproportionation and the rate constant for the reaction between the Mo(IV) complex and HN_3. Since the former can reasonably be expected to be less than 1, as is the case in chlorobenzene,[18] it follows that the reaction using $Mo_2O_3(S_2CNEt_2)_2$ should provide somewhat lower yields of N_2 after 3 min than the corresponding reaction which started with $MoO(S_2CNEt_2)_2$ alone. It also follows that the initial presence of $MoO_2(S_2CNEt_2)_2$ should retard the rate of the reaction. Both of these requirements are observed.

Possible Biological Significance. Although the reactions which have been reported herein require HN_3 rather than N_3^- for rapid electron transfer, it is unlikely that the reaction of azide with nitrogenase requires HN_3 due to pH restrictions. In fact, the nitrogenases from *A. vinelandii* and *C. pasteurianum* reduce azide effectively at pH 7.[6] If it is assumed that Mo(IV) is the active, reduced form of molybdenum in the nitrogenases, these results do not preclude the possibility that activation of N_3^- in the biological systems occurs by way of specific hydrogen bonding to a nearby X–H group as shown below. However, there is at least one Mo(IV) complex, *trans*-$MoO(OH_2)(CN)_4^{2-}$, which will reduce azide in nearly neutral solutions.[20] The effect of the acidity of the solution is not known in that case.



Furthermore, the results obtained with $Mo_2O_3(S_2CNEt_2)_4$ suggest that disproportionation may be a viable pathway to Mo(IV) in the enzymic systems as previously suggested.[3,13]

Experimental Section

Materials and Instrumentation. The sodium salts of the dithiocarbamates were prepared by condensation of the appropriate amines with CS_2 in basic media. The compounds, $MoO(S_2CNEt_2)_2$ and $MoO(S_2CN(i\text{-}Pr)_2)_2$, were prepared by reduction of $MoO_2(S_2CNR_1R_2)_2$ with aqueous dithionite solutions.[21] Due to failure of this method, $MoO(S_2CN(Me)_2)_2$ and $MoO(S_2CN(Me)(Bz))_2$ were prepared by reduction of the corresponding Mo(VI) compounds with thiophenol[4] or triphenylphosphine.[5] Each afforded identical results. Pertinent aspects of the infrared spectra of these compounds are included in Table I. A weak absorption at 953 cm^{-1} in the spectrum of $MoO(S_2CN(Me)(Bz))_2$ is not due to a second isomer, although permitted by the structure, since an absorption at an identical frequency is also present in the spectrum of the sodium salt of the ligand. The synthesis of $MoO(S_2CN(Bz)_2)_2$ was unsuccessful by either route. Each yielded only $Mo_2O_3(S_2CN(Bz)_2)_4$. Literature methods were used to prepare both $MoCl_2(S_2CNEt_2)_2$ and $MoOCl_2(S_2CNEt_2)_2$.[11] Purity was confirmed from their infrared spectra. The dinuclear complex, $Mo_2O_3(S_2CNEt_2)_4$, was prepared from stoichiometric quantities of MoO_4^{2-}, $S_2CNEt_2^-$, and dithionite in aqueous solution. Absorptions due to either $MoO_2(S_2CNEt_2)_2$ or $MoO(S_2CNEt_2)_2$ were not observed in the infrared spectrum of the compound. All reactions were performed either under argon or in vacuo. Organic solvents were dried and distilled immediately before use.

Infrared spectra were recorded using a Perkin-Elmer Model 283 spectrophotometer and Nujol mulls. Electronic spectra were measured with a Cary Model 14 spectrophotometer. Mass spectra were obtained with a Varian CH-7 mass spectrometer. Titrations were accomplished using a Corning Digital 109 pH meter. Gases were collected by using a Toepler pump.

Reactions of $MoO(S_2CNR_1R_2)$ with Azide. In a typical reaction, 1.25 mmol of the Mo(IV) compound was added to a flask of known volume containing 10 mL of oxygen-free, aqueous HCl of known concentration. A side arm contained 6.13 mmol of NaN_3. After the system was evacuated, 25 mL of dried, distilled $CHCl_3$ was added. The system was then attached to the Toepler line through an intervening stopcock and stirred. The initial time was taken to be the addition of NaN_3 from the side arm. After exactly 3 min, the stopcock was closed and the volume of N_2 within the closed system was measured. The total amount of N_2 which was liberated was calculated from the known total volume of the system. The mass spectrum confirmed that the gas was N_2 while the Nessler reaction confirmed the presence of NH_4^+. The yields of ammonia, when measured by this reaction and also by the quantity of N_2 produced by the quantitative oxidation of NH_3 by NaOBr, were corrected for the presence of small quantities of decomposition products from the ligand.[22] This correction was determined from solutions which were exposed to the normal reaction conditions but with azide ion absent in the aqueous layer. However, the correction is essentially unnecessary since it never amounted to more than 0.1 mol/mol of complex under these conditions. Products which contained molybdenum were isolated and characterized from their spectra. Reactions were conducted at the temperature of the laboratory which was approximately 23 °C.

Extraction Studies. These were conducted in a manner which is identical with that described above but in the absence of the Mo(IV) complexes. A 10-mL aliquot which was removed from the organic layer after 3 min was treated with 10 mL of 1 M HCl containing excess

Ce(IV). After the evolution of N_2 was complete, the volume of the gas was measured.

Acknowledgment. This research was supported by the National Science Foundation through Grant MPS-75-08188.

Registry No. $MoO(S_2CN(CH_3)_2)_2$, 39587-09-2; $MoO(S_2CN(CH_3)(C_6H_5CH_2))_2$, 65452-63-3; $MoO(S_2CN(C_2H_5)_2)_2$, 25395-92-0; $MoO(S_2CN(i\text{-}C_3H_7)_2)_2$, 65483-45-6; $[(n\text{-}C_3H_7)_4N]N_3$, 993-21-5; N_2, 7727-37-9; NH_3, 7664-41-7.

References and Notes

(1) P. C. H. Mitchell and R. D. Scarle, *J. Chem. Soc., Dalton Trans.*, 2552 (1975).

(2) P. W. Schneider, D. C. Bravard, J. W. McDonald, and W. E. Newton, *J. Am. Chem. Soc.*, **94**, 8640 (1972).

(3) W. E. Newton, J. L. Corbin, D. C. Bravard, J. E. Searles, and J. W. McDonald, *Inorg. Chem.*, **13**, 1100 (1974).

(4) J. W. McDonald, J. L. Corbin, and W. E. Newton, *Inorg. Chem.*, **15**, 2056 (1976).

(5) G. J.-J. Chen, J. W. McDonald, and W. E. Newton, *Inorg. Chem.*, **15**, 2612 (1976).

(6) R. W. F. Hardy and E. Knight, *Biochim. Biophys. Acta*, **139**, 69 (1967).

(7) Although $MoO(S_2CNEt_2)_2$ reacts with $CHCl_3$ in an unknown manner to produce $MoOCl_2(S_2CNEt_2)_2$,[5] unpublished studies in this laboratory by B. Marks have shown that the oxidation of the Mo(IV) complex by the solvent occurs far more slowly than the oxidation by azide. Consequently, the solvent-dependent oxidation of the complex does not compete with the oxidation by azide during this period of time.

(8) L. Ricard, J. Estienne, P. Karagiannidis, P. Toledano, J. Fischer, A. Mitschler, and R. Weiss, *J. Coord. Chem.*, **3**, 277 (1974).

(9) E. P. Clark, *Anal. Chem.*, **13**, 820 (1941).

(10) P. R. Robinson, E. O. Schlemper, and R. K. Murmann, *Inorg. Chem.*, **14**, 2035 (1975).

(11) W. E. Newton, D. C. Bravard, and J. W. McDonald, *Inorg. Nucl. Chem. Lett.*, **11**, 553 (1975).

(12) J. Dirand, L. Ricard, and R. Weiss, *J. Chem. Soc., Dalton Trans.*, 278 (1976).

(13) R. A. D. Wentworth, *Coord. Chem. Rev.*, **18**, 1 (1976).

(14) J. Chatt, L. A. Duncanson, and L. M. Venanzi, *Suom. Kemistil. B*, **29**, 75 (1956).

(15) E. A. Pasek and D. K. Straub, *Inorg. Chem.*, **11**, 259 (1972).

(16) B. J. McCormick, *Inorg. Chem.*, **7**, 1965 (1968).

(17) F. W. Moore and M. L. Larson, *Inorg. Chem.*, **6**, 998 (1967).

(18) R. Barral, C. Bocard, I. Seree de Roch, and L. Sajus, *Tetrahedron Lett.*, 1693 (1972).

(19) J. W. McDonald, private communication.

(20) G. N. Schrauzer, P. R. Robinson, E. L. Moorehead, and T. M. Vickrey, *J. Am. Chem. Soc.*, **97**, 7069 (1975).

(21) R. N. Jowitt and P. C. H. Mitchell, *J. Chem. Soc. A*, 2632 (1969).

(22) R. E. E. Hill and R. L. Richards, *Nature (London)*, **233**, 114 (1971).

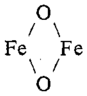
Contribution from the School of Chemical Sciences,
University of Illinois, Urbana, Illinois 61801

Reaction of μ-Oxo-Bridged Iron(III) Complexes with Organic Acids: A Characterization of the Products

RONALD G. WOLLMANN and DAVID N. HENDRICKSON*[1]

Received February 14, 1977

The products from the reactions of μ-oxo-bis(*N,N'*-ethylenebis(salicylideniminato)iron(III)), $[Fe(salen)]_2O$, with trichloroacetic acid (tcaH), trifluoroacetic acid (tfaH), salicylic acid (salH), picric acid (picH), and picolinic acid (picH) are characterized. Dimeric compounds of composition $[Fe(salen)X]_2$ are obtained where X is tca⁻, tfa⁻, sal⁻, or pic⁻. A monomeric compound of composition Fe(salen)X is obtained when X is pico⁻. Monomeric compounds of composition Fe(TPP)(X) are obtained from the reaction of μ-oxo-bis(tetraphenylphyrinato)iron(III)), $[Fe(TPP)]_2O$, with picH and tcaH. An antiferromagnetic exchange interaction is indicated by variable-temperature (4.2–267 K) magnetic susceptibility data for the dimeric salen compounds. Exchange parameters, J, in the range of -4.5 to -7.0 cm^{-1} are obtained for the dimers by least-squares fitting of the data to the theoretical equation for an isotropic exchange interaction ($\hat{H} = -J\hat{S}_1\cdot\hat{S}_2$) for $S_1 = S_2 = {}^5/_2$ with the inclusion of a monomeric ferric impurity. Iron-57 Mössbauer parameters are reported for Fe(salen)(pico) and $[Fe(salen)(tfa)]_2$. X-Band (8–300 K) and Q-band (100–300 K) EPR spectra are presented. Very complex EPR spectra at 90 K are obtained for the $[Fe(salen)X]_2$ compounds. No EPR signals are observed at 8 K for the dimeric compounds in the X-band spectra. Infrared spectra at ~30 and 300 K are reported. An absorption in the 850-cm^{-1} region is observed for Fe(salen)(pico) as well as for each $[Fe(salen)X]_2$ compound. These absorptions are tentatively assigned to the asymmetric stretching vibration for the moiety



Introduction

The equilibria and reactions involved in the formation and dissociation of μ-oxo-bridged iron(III) complexes are known to be complicated and are not totally understood.[2-6] Mechanisms have been proposed[4] which involve various dimeric species such as di-μ-hydroxo-, μ-alkoxo-μ-hydroxo-, μ-halo-μ-hydroxo-, μ-aquo-μ-hydroxo-, and di-μ-halo-bridged iron(III) complexes. Several di-μ-alkoxo-[7-10] and di-μ-hydroxo-bridged[11,12] iron(III) dimers have been isolated and characterized.

Organic acids react with μ-oxo-bridged iron(III) complexes. In this paper we report the synthesis and characterization of the reaction products of several organic acids with μ-oxo-bis(tetraphenylporphyrinatoiron(III)), $[Fe(TPP)]_2O$, and μ-oxo-bis(*N,N'*-ethylenebis(salicylideniminato)iron(III)), $[Fe(salen)]_2O$.

Results and Discussion

The reaction of a CH_3Cl solution of $[Fe(salen)]_2O$ with certain organic acids has been found to give compounds with the composition of Fe(salen)X, where X⁻ is variously the monoanion of trichloroacetic acid (tcaH), trifluoroacetic acid (tfaH), salicylic acid (salH), picric acid (picH), or picolinic acid (picoH). In the following sections it will be shown that, except for the picolinic acid compound, these compounds are dimers, $[Fe(salen)X]_2$. On the other hand, it will be shown that the similarly prepared Fe(TPP)X compounds, where X⁻ is the monoanion of trichloroacetic or picric acid, are probably monomeric.

Magnetic Susceptibility Measurements. Variable-temperature (4.2–270 K) magnetic susceptibility data were collected for the five Fe(salen)X compounds and also for

0020-1669/78/1317-0926$01.00/0