sition product. Since it is present in spectra recorded in various solvents and from samples synthesized by various methods, this peak does not appear to be caused by impurity. It is close to the 1910-cm^{-1} position predicted[8] for the silent A_2 mode of II from the overtone and combination bands. This peak cannot be assigned as the ^{13}C satellite of the B_u band of III which has been observed at 1924 cm^{-1} in nonane solutions of $[CpFe(CO)_2]_2$.[10] This band could be the ^{13}C satellite of the A_u or B_u modes of IV, but they probably occur at higher frequencies. Whereas the relative intensities of the three higher frequency bands cannot be rationalized with a reasonable C_{2v} geometry,[29] the relative intensities of the highest and lowest frequency bands (ratio between $^4/_1$ and $^{10}/_1$) of the nonbridged forms are consistent with reasonable staggered structures. Assuming that IV and V are present in comparable quantities, probably in a $^2/_1$ or $^3/_1$ ratio, the lack of temperature dependence in the carbonyl bands indicates that the ΔH_4 must be less than 0.2 kcal/mol.

The equilibrium in $[CpM(CO)_2]_2$ compounds thus involves four isomers for ruthenium and presumably also for iron: I $\rightleftarrows$ V $\rightleftarrows$ IV $\rightleftarrows$ III. These equilibria have been investigated in nonpolar solvents and the results referenced to isomer I as given in Table III. ΔH_2 and ΔS_2 have been calculated from the values reported by Noack[10] assuming ΔH_1, ΔS_1, and the relative extinction coefficients in Table II. Since ΔH_2 for $[CpRu(CO)_2]_2$ is 3 kcal/mol less than ΔH_2 for $[CpFe(CO)_2]_2$, ΔH_3 of $[CpRu(CO)_2]_2$ has been estimated as 9 kcal/mol; interconversion of all four isomers is expected to be rapid on the nmr time scale even at −100°. The barrier ΔH_5 between IV and the polar nonbridged form, probably V, can be no greater than 8 kcal/mol and is probably much less. The rapid interconversion of IV and V may be fast even on the ir time scale. $[CpOs(CO)_2]_2$ would provide a better vehicle for structural studies of IV and V, for it should show this fast equilibrium uncomplicated by the presence of I or III.

TABLE III

THERMODYNAMIC PARAMETERS FOR $[CpM(CO)_2]_2$

	Fe	Ru
$\Delta H_1{}^a$	0.9 ± 0.1	~1
$\Delta S_1{}^b$	3.5 ± 0.5	~3
$\Delta H_2{}^{a,c}$	4.9 ± 1	1.7 ± 0.5
$\Delta S_2{}^{b,c}$	6.5 ± 2	6.9 ± 1
$\Delta H_3{}^a$	~12	~9
$\Delta S_3{}^b$	~0	~0
$\Delta H_4{}^a$	. . .	<0.2
$\Delta H_5{}^a$	. . .	<8

[a] In kcal/mol. [b] In eu. [c] Recalculated from ref 10 assuming ΔH_1 and ΔS_1.

Conclusions

The immediate conclusion reached by this work is that a four-structure model as shown in Figure 3 best describes the potential energy surfaces available to $[CpFe(CO)_2]_2$ and $[CpRu(CO)_2]_2$. Internally consistent, complementary results obtained by infrared and nmr spectroscopy allow us to identify the different isomers present in solution and yield quantitative kinetic and thermodynamic data necessary to map out accurately areas of the potential energy surface. This quantitative information also strongly supports a mechanism whereby cis- and trans-CO-bridged isomers can interconvert *via* nonbridged isomers: I $\rightleftarrows$ V $\rightleftarrows$ IV $\rightleftarrows$ III. Thus, we furnish the first strong proof that bridged–nonbridged structure interconversions, of the type shown in eq 1, occur with low activation energy. Examination of the chemical literature as well as other results obtained in this laboratory indicate that this type of rearrangement may occur with great generality in metal carbonyl chemistry and may thus provide a basis for an extensive class of stereochemically nonrigid and fluxional molecules.

[29] The angle between the carbonyls bound to the same metal is calculated to be about 90°, but the dihedral angle between the $Ru(CO)_2$ planes is calculated to be about 140° which would crowd the cyclopentadienyl rings excessively.

CONTRIBUTION FROM THE CHEMISTRY DEPARTMENT, THE UNIVERSITY OF ARIZONA,
TUCSON, ARIZONA 85721, AND BELL LABORATORIES, MURRAY HILL, NEW JERSEY 07971

The Spectra of Bis(tertiary arsine) Complexes. III.[1a] Tetragonal Iron(III)

BY ROBERT D. FELTHAM,*[1b] W. SILVERTHORN,[1b,c] H. WICKMAN,[1d] AND W. WESOLOWSKI[1b,e]

Received September 21, 1971

The magnetic susceptibilities, electron spin resonance, and Mössbauer spectra of the complexes *trans*-$[FeX(NO)(das)_2]^+$ and *trans*-$[FeX_2(das)_2]^+$ have been obtained. These complexes have one unpaired electron per iron, with magnetic moments ranging from 1.81 to 2.31 BM at room temperature. The Mössbauer spectra consist of quadrupole-split doublets with the quadrupole splitting ranging from 2.2 to 2.5 mm/sec for *trans*-$[FeX_2(das)_2]^+$ and being 1.0 mm/sec for *trans*-$[FeX(NO)(das)_2]^+$. Both the magnetic susceptibilities and esr spectra show that the *trans*-$[FeX(NO)(das)_2]^+$ complexes have rhombic fields, while the *trans*-$[FeX_2(das)_2]^+$ compounds are tetragonal. These data can be accommodated by the ligand field model for Fe(III) in rhombic or tetragonal fields.

Introduction

The electronic structure of nitrosyl complexes has been investigated by several authors.[2-4] The previous investigators have dealt with transition metal nitrosyl complexes in which the M–N–O grouping was linear or

---

(1) (a) Part II: R. D. Feltham and W. Silverthorn, *Inorg. Chem.*, **9**, 1207 (1970). (b) University of Arizona. (c) Shell Fellow, 1966–1967. (d) Bell Laboratories. (e) Ethyl Corp. Fellow, 1970–1971.

(2) P. T. Manoharan and H. B. Gray, *Inorg. Chem.*, **5**, 823 (1966).

(3) J. Danon, *J. Chem. Phys.*, **41**, 3378 (1964).

(4) B. Jezowska-Trezebiatowska, "Theory and Structure of Complex Compounds," Macmillan, New York, N. Y., 1964.

thought to be linear. Recent structural data[5-7] have shown that there are also numerous transition metal complexes of nitric oxide in which the M–N–O bond angle is as small as 120°. Transition metal complexes of NO in which the bond angle is approximately 120° clearly must have electronic structures which differ markedly from those found for the linear M–N–O complexes. The relationships between bond angle (structure) and bonding may be interpreted in several different ways ($N{\equiv}O^+$ *vs.* $N{=}O^-$, for example) and a definitive assignment of the correct electronic configuration(s) may be elusive. For the iron complexes described below, this problem was attacked by comparison of the ligand field effects (as evidenced by Mössbauer spectroscopy and magnetic susceptibility) in *trans*-$[FeX_2(das)_2]^+$ complexes and the related *trans*-$[FeX(NO)(das)_2]^+$ complexes. The results are considered in terms of a standard ligand field scheme in which a strong-field NO^- group is coordinated to the iron. In this sense, the data support a π-bonded $N{=}O^-$ model of the NO group.

Experimental Section

The complexes were prepared as reported elsewhere.[8,9] The visible and near-infrared spectra were obtained in solution by use of a Cary Model 14. The diffuse reflectance spectra of the solids were obtained from a Zeiss PMQ II spectrometer using a photomultiplier for the ultraviolet and visible regions and a PbS detector for the near-infrared region. Lithium fluoride powder, obtained from K & K Laboratories, was used as a reference over the entire spectral region. The reflectance data obtained were converted to the logarithmic form of the Kubelka–Munk function[10] and plotted *vs.* energy (kK).

The Mössbauer spectra were obtained from 300 to 4.2°K using a ^{57}Co–Pd source. The magnetic susceptibility measurements from 77 to 300° were carried out using a Faraday balance of a design similar to that described by Hatfield[11a] and Figgis.[11b] The magnetic susceptibility from 1.2 to 77° was obtained using a null-coil pendulum magnetometer based on a design by Bozorth, *et al.*[12]

Results and Discussion

Halide Complexes of Fe(III).—The complexes $[FeCl_2(das)_2]^+$ and $[FeBr_2(das)_2]^+$ (das is *o*-phenylenebis(dimethylarsine)) were first prepared by Nyholm,[9] who showed that these complexes have only one unpaired electron per cation. The magnetic moment measured at room temperature was 2.31 BM for the chloride. This rather high value for the magnetic susceptibility is consistent with the value expected for spin-paired iron(III) complexes with a t_{2g}^5 configuration.[13] In an octahedral complex, the ground electronic state would be $^2T_{2g}$. However, the low symmetry of these complexes will certainly give rise to an additional splitting of the octahedral ground state, $^2T_{2g}$. To understand further the magnetic properties of these iron complexes, it was necessary to elucidate their stereochemistry.

Single-crystal X-ray diffraction experiments have shown that in salts of the green complex ion $[CoCl_2(das)_2]^+$ the ligands about the cobalt ion have a trans arrangement.[14] Although there have been no single-crystal studies of the iron complexes, X-ray powder patterns of perchlorate salts of both *trans*-$[CoCl_2(das)_2]^+$ and -$[FeCl_2(das)_2]^+$ have been obtained. These powder patterns show that the cobalt and iron salts are isomorphous. In addition, the $-CH_3$ rocking motions near 900 cm^{-1} in six-coordinate complexes containing two *o*-phenylenebis(dimethylarsine) ligands have been shown to be very sensitive to the steric arrangement of atoms around the central metal ion.[15] The infrared spectra of *trans*-$[CoCl_2(das)_2]^+$ and *trans*-$[FeCl_2(das)_2]^+$ are nearly identical. The nmr spectral differences between the cis and trans isomers are quite characteristic and have been reliably used to identify these isomers in complex ions[16] with the composition $[MX_2(das)_2]^+$.

All of the preparations of the $[FeCl_2(das)_2]^+$ and $[FeBr_2(das)_2]^+$ complexes gave only the trans isomers. There was no evidence (X-ray, infrared, or visible spectra) for the presence of any of the cis isomers in these compounds. The magnetic susceptibility of *trans*-$[FeBr_2(das)_2]ClO_4$ and *trans*-$[FeCl_2(das)_2]ClO_4$ was measured from 77 to 300°K. The results of these measurements are summarized in Table I. The magnetic moment of these complexes varies from 2.04 BM at low temperatures to 2.31 BM at room temperature. These values for the magnetic susceptibility are compatible with spin-paired complexes of Fe(III) in a tetragonal field. The discussion which follows will assume a local symmetry of D_{4h} and any important deviations from D_{4h} symmetry will be treated separately.

TABLE I

EXPERIMENTAL MAGNETIC MOMENTS OF $[Fe(das)_2XX']^+$

Temp, °K	μ, BM	Temp, °K	μ, BM	Temp, °K	μ, BM	Temp, °K	μ, BM
$[Fe(das)_2Cl_2]ClO_4$				$[Fe(das)_2Br_2]ClO_4$			
86.8	2.12	183.7	2.22	78.9	2.07	204.8	2.18
104.0	2.14	203.6	2.25	99.2	2.08	215.9	2.18
126.2	2.17	217.1	2.26	121.7	2.10	231.3	2.19
139.7	2.18	231.9	2.27	147.0	2.12	245.4	2.21
165.7	2.20	298.6	2.31	165.0	2.15	258.2	2.21
				181.0	2.16	298.0	2.24
$[Fe(das)_2ClNO]ClO_4$				$[Fe(das)_2BrNO]ClO_4$			
101.4	1.77	187.0	1.78	88.4	1.88	176.8	1.90
124.4	1.78	202.7	1.78	147.8	1.91	184.7	1.92
150.8	1.78	217.6	1.78	158.2	1.93	296.5	1.93
168.0	1.78	294.9	1.81				

The term which is lowest in energy in a ligand field of D_{4h} symmetry will depend upon the relative energies of the d_{xy} and the d_{xz}, d_{yz} orbitals. If the d_{xz}, d_{yz} orbitals are lower in energy than the d_{xy} orbital, then the electron configuration in a *strong tetragonal field* would be $(d_{xz}, d_{yz})^4d_{xy}$ and the $^2B_{2g}$ state would be lowest in energy. If the d_{xy} orbital is lowest in energy, then the strong field configuration would be $d_{xy}^2(d_{xz}, d_{yz})^3$, and the ^2E_g state would be lowest in energy. The sign and magnitude of the splitting of the $^2T_{2g}$ term (and hence the correct ground state) may in favorable cases be de-

---

(5) D. J. Hodgson and J. A. Ibers, *Inorg. Chem.*, **7**, 2345 (1968).

(6) G. R. Davies, R. H. B. Mais, and P. G. Owston, *Chem. Commun.*, 81 (1968).

(7) J. H. Enemark and R. D. Feltham, *J. Chem. Soc.*, in press.

(8) W. Silverthorn and R. D. Feltham, *Inorg. Chem.*, **6**, 1662 (1967).

(9) R. S. Nyholm, *J. Chem. Soc.*, 851 (1950).

(10) W. W. Wendlandt and H. Hect, "Reflectance Spectroscopy," Intescience, New York, N. Y., 1966.

(11) (a) W. E. Hatfield, C. S. Fountain, and R. Whyman, *Inorg. Chem.*, **5**, 1855 (1966); (b) B. N. Figgis and R. S. Nyholm, *J. Chem. Soc.*, 331 (1959).

(12) R. M. Bozorth, H. J. Williams, and D. E. Walsh, *Phys. Rev.*, **103**, 572 (1956).

(13) B. N. Figgis, "Introduction to Ligand Fields," Interscience, New York, N. Y., 1966, Chapter 10.

(14) P. J. Pauling, D. W. Porter, and G. B. Robertson, *J. Chem. Soc.*, 2728 (1970).

(15) G. B. Deacon and J. H. S. Green, *Spectrochim. Acta, Part A*, **24**, 959 (1968).

(16) B. D. W. Baylis and J. C. Bailar, Jr., *Inorg. Chem.*, **9**, 641 (1970).

termined from analysis of magnetic susceptibility data and Mössbauer spectra.[13,17]

The susceptibility of *trans*-$[FeBr_2(das)_2]^+$ varies from 1.8 BM at 4°K to 2.24 BM at 300°K, while that of *trans*-$[FeCl_2(das)_2]^+$ varies from 2.12 BM at 77°K to 2.31 BM at 300°K. These data are consistent with a spin-paired Fe(III) complex with a t_{2g}^5 electron configuration and a small splitting of the $^2T_{2g}$ ground state by a tetragonal field.

Using a computer-fitting procedure similar to that developed by Gerloch,[18] the experimental temperature-dependent magnetic moments were compared to theoretical moments derived from the tetragonally distorted $^2T_2$ model of Figgis.[19] By this technique, both the *trans*-$[FeCl_2(das)_2]^+$ and *trans*-$[FeBr_2(das)_2]^+$ may be assigned $^2B_2$ ground terms with values for the tetragonal distortion (Δ) of approximately 750 and 1000 cm^{-1}, respectively. The electron delocalization factor (k) was found to be unity, but the spin–orbit coupling constant, λ, appears reduced by 5–10%.

The Mössbauer spectra of the tetragonal complexes $[FeX_2(das)_2]^+$ were measured over the temperature range from 4.2 to 300°K. The results of these measurements are reported in Table II. At 4.2°K the Mössbauer spectra of all of these complexes consist of a quadrupole-split doublet with a quadrupole splitting ranging from 1 mm/sec in the nitrosyl complexes to 2.5 mm/sec in $[FeBr_2(das)_2]ClO_4$ with isomer shifts of 0.1 and 0.2 mm/sec, respectively. The quadrupole splitting observed in the Mössbauer spectrum of $[FeBr_2(das)_2]^+$ and $[FeCl_2(das)_2]^+$ decreases from 2.5 mm/sec at 4°K to 2.2 mm/sec at 300°K. This small decrease in the quadrupole splitting may be attributed to an increase in population of the partner level of the $^2T_{2g}$ state. This implies a splitting of the latter term by greater than 300 cm^{-1}. The lattice contribution to the net EFG is not expected to change greatly among the present compounds, and all major changes are assigned to varying electronic factors, *i.e.*, to the details of the ground electronic level.

TABLE II

MÖSSBAUER QUADRUPOLE SPLITTINGS (QS), ISOMER SHIFTS (IS) FOR THE IRON COMPLEXES

	$[FeBr_2(das)_2][ClO_4]$		
Temp, °K	300	77	4.2
QS, mm/sec	2.23	2.48	2.48
IS, mm/sec	0.14	0.24	0.24
	$[FeCl_2(das)_2][ClO_4]$		
Temp, °K	300	86.8	4.2
QS, mm/sec	2.24	2.44	2.46
IS, mm/sec	0.12	0.20	0.20
	$[FeBrNO(das)_2][ClO_4]$		
Temp, °K	300	93.4	4.2
QS, mm/sec	. . .[a]	1.04	1.04
IS, mm/sec	. . .[a]	0.12	0.12

[a] The unusually low recoil-free fraction, together with the bromine absorption, precluded an accurate Mössbauer measurement at room temperature.

It was shown in previous studies that *o*-phenylenebis(dimethylarsine) occupies about the same position in the spectrochemical series as ethylenediamine[20] and is well above the halides in this series. Thus for *trans*-$[FeCl_2(das)_2]^+$ and *trans*-$[FeBr_2(das)_2]^+$ the axial field of the halides is weaker than that of the four arsenic ligand atoms in the xy plane. If large π-bonding effects are absent, then the d_{xz}, d_{yz} orbitals will lie lower in energy than the d_{xy} orbital. This ordering of orbital energies would in turn lead to the ground state in tetragonal symmetry of $^2B_{2g}$. This ordering is also supported by detailed calculations.[21]

Employing the greatly simplified model of Ingalls,[22] the approximate ordering of the nuclear spin levels for the various ground states available to a spin-paired Fe(III) ion may be obtained. These calculations show that the relative energies of the $m_I = \pm{}^3/_2$ levels *vs.* the $m_I = \pm{}^1/_2$ levels will be reversed in going from a $^2B_{2g}$ to a ^2E_g ground state. Moreover, the energy separation between these two nuclear levels will differ by a factor of 2: $\Delta E(^2B_{2g}) = 2\Delta E(^2E_g)$, where ΔE is the energy separation between the $m_I = \pm{}^3/_2$ and $m_I = \pm{}^1/_2$ levels. With the more complete model of Golding,[23] the nuclear quadrupole splitting may be computed as a function of Δ (tetragonal distortion), k (electron delocalization), and λ (spin–orbit coupling). The ratio $\Delta E(^2B_{2g})/\Delta E(^2E_g)$ as a function of $|\Delta/\lambda|$ is given in Figure 1. It is clear that the relationship $\Delta E(^2B_{2g}) = 2\Delta E(^2E_g)$ as predicted by the simplified model of Ingalls is closely approximated for systems with $|\Delta/\lambda| > 1.5$. Although the sign of the quadrupole splitting parameter has not been determined, the magnitude of the quadrupole splitting and the isomer shift corresponds to that observed in other tetragonal spin-paired complexes of iron(III).[17] The isomer shifts which have been observed for tetragonal spin-paired iron(III) complexes range from 0.2 mm/sec in $Na_2[Fe(CN)_5P(C_6H_5)_3]$ to 0.5 mm/sec in iron(III) phthalocyanine chloride. The magnitude of the quadrupole splitting is also within the range found for these spin-paired tetragonal complexes of iron(III), being 1.4 mm/sec for $Na_2[Fe(CN)_5P(C_6H_5)_3]$ and almost 3.0 mm/sec for iron(III) phthalocyanine chloride.

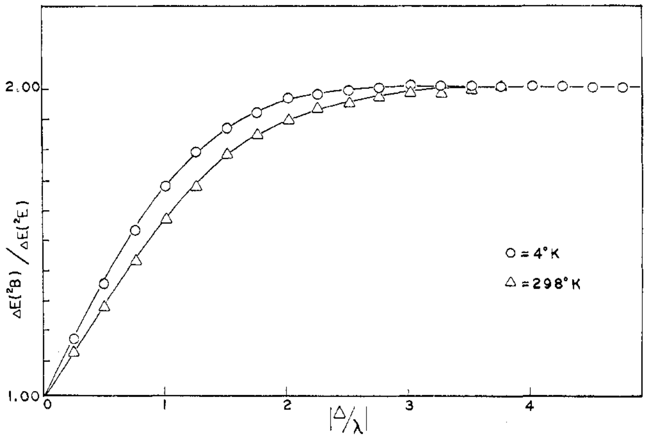

Figure 1.—Theoretical ratio of the quadrupole splitting for the ^2B and ^2E components of the tetragonal field (Δ).

Nitrosyl Complexes of Iron(III).—The compounds with the composition $[FeX(NO)(das)_2][ClO_4]$ have been reported previously.[8] These complexes have

---

[17] V. I. Goldanskii and R. Herber, "Chemical Applications of Mössbauer Spectroscopy," Academic Press, New York, N. Y., 1968.

[18] M. J. Gerloch, *J. Chem. Soc. A*, 2037 (1968).

[19] B. N. Figgis, *Trans. Faraday, Soc.*, **57**, 190 (1961).

[20] R. D. Feltham and W. Silverthorn, *Inorg. Chem.*, **7**, 1154 (1968).

[21] W. Silverthorn, Ph.D. Dissertation, University of Arizona, 1967.

[22] R. Ingalls, *Phys. Rev. A*, **133**, 787 (1964).

[23] R. M. Golding, *Mol. Phys.*, **12**, 13 (1967).

ground states with one unpaired electron per iron, $S = {}^1/_2$. X-Ray powder patterns have shown that the compounds $[FeClNO(das)_2][ClO_4]$ are essentially isomorphous with the *trans*-$[CoCl_2(das)_2][ClO_4]$ compound. Recently, a single crystal of this compound has been examined by X-ray diffraction techniques.[24] Although the chloride and nitrosyl groups disorder as they must to be isomorphous with *trans*-$[CoCl_2(das)_2][ClO_4]$, the trans arrangement of the chloride and nitrosyl ligands has been confirmed. In addition, although the measurements are not accurate due to the disorder problem, the Fe–N–O bond angle is approximately 148°. While many other transition metal complexes with an M–N–O angle of less than 180° also have structures plagued with disorder problems, Ibers[5] has reported a structure in which the M–N–O bond angle is 120° and the NO group is ordered in the crystal.

Regarding the NO group as a strong-field ligand, we see that there is an important difference, however, between $[FeCl_2(das)_2]^+$ and $[FeCl(NO)(das)_2]^+$. The nitrosyl group dominates the bonding with the metal in most of its transition metal complexes and is usually placed near the cyanide ligand in the spectrochemical series. Consequently the axial field will be stronger than the field of the four arsenic ligand atoms in the xy plane. Thus the splitting of the ${}^2T_{2g}$ state will be of opposite sign to that for $[FeCl_2(das)_2]^+$. In a strong tetragonal field, the electron configuration for $[FeCl(NO)(das)_2]^+$ should be $d_{xy}{}^2(d_{xy}, d_{yz})^3$ which would give rise to a ${}^2E$ ground state.

However, all attempts to fit the temperature-dependent magnetic moments (Table I) of *trans*-$[FeCl(NO)(das)_2]^+$ and *trans*-$[FeBr(NO)(das)_2]^+$ to a tetragonal model failed to provide any successful assignment of the ground state. Because the observed g tensor is rhombic ($g_z \neq g_y \neq g_z$),[25] a rhombic (D_{2h}) model was used to calculate theoretical moments as a function of field distortion, spin–orbit coupling, and electron delocalization.[26] Although complete computer fitting was not performed, the nearly spin-only behavior is compatible with only a rhombically distorted ${}^2E$ ground term. More importantly, the quadrupole splitting in the Mössbauer spectrum for spin-paired, tetragonally distorted iron(III), ${}^2B_2$, should be 1.5 times the quadrupole splitting for the rhombically distorted iron(III), ${}^2E$. Rhombic distortion of the ${}^2B$ ground term produces a system with no quadrupole splitting.[26] The data in Table II show the quadrupole splitting in *trans*-$[FeBr_2(das)_2]^+$ to be approximately 2.4 times that found for *trans*-$[FeBr(NO)(das)_2]^+$.

Conclusions

These studies have shown that both *trans*-$[FeX_2(das)_2]^+$ and *trans*-$[FeX(NO)(das)_2]^+$ can be treated as complexes of Fe(III). This implies that the NO group has two electrons more than are present in the $N{\equiv}O^+$ group, leaving the nitrosyl group with one negative charge. This point of view is consistent with the low NO stretching frequencies and the small bond angles of these iron nitrosyl complexes. The magnetic susceptibility indicates that there is a tetragonal splitting of the ${}^2T_{2g}$ ground state of *trans*-$[FeX_2(das)_2]^+$ and a rhombic splitting in the nitrosyl complexes. The Mössbauer spectra show that the field is of opposite sign in the nitrosyl and the dihalides as is predicted by a simple ligand field model.

Acknowledgment.—Portions of this work were supported by the National Science Foundation.

---

[24] R. W. Perry, Ph.D. Dissertation, University of Wisconsin, 1968.

[25] H. Crain and R. D. Feltham, unpublished results.

[26] W. Wesolowski, Ph.D. Dissertation, University of Arizona, 1971.

CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, UNIVERSITY OF CALIFORNIA,
SANTA BARBARA, CALIFORNIA 93106

Kinetics of Ruthenium(II) Substitution Reactions. Reaction of Aquopentaammineruthenium(II) with Various Pyridines and Organonitriles[1]

BY REBECCA J. ALLEN AND PETER C. FORD*

Received June 8, 1971

Substitution rates for the complex ion $Ru(NH_3)_5H_2O^{2+}$ are reported for replacement of the labile coordinated water by various substituted pyridines and by several organonitriles (acetonitrile, benzonitrile, perfluorobenzonitrile, and 3- and 4-cyanopyridine). Over considerable ligand concentration ranges, the reactions obey the second-order rate law $d[Ru(NH_3)_5L^{2+}]/dt = k_L[Ru(NH_3)_5H_2O^{2+}][L]$ with rate constant k_L ranging from 0.048 to 0.32 M^{-1} sec^{-1} (25°) depending on the nature of L and certain media conditions. The 3- and 4-substituted pyridines follow a reactivity order parallel to their basicities, electron-withdrawing substituents decreasing the rate and electron-donating substituents increasing the rate; however, the rate differences are small, a fact which is interpreted as implying an SN1 (dissociative) substitution mechanism. The organonitriles generally react more rapidly than do the pyridines. The rates and activation parameters for all these reactions are compared with similar data previously reported for the reactions of $Ru(NH_3)_5H_2O^{2+}$ with N_2, N_2O, and $Ru(NH_3)_5N_2{}^{2+}$ and interpreted in terms of two transition state features: steric effects and the nature of the developing metal–ligand bond.

Introduction

During the past several years, a number of new pentaammineruthenium(II) complexes of π-unsaturated ligands, $Ru^{II}(NH_3)_5L$, have been described. These ligands (L) include aromatic nitrogen heterocycles such as pyridine,[2] organonitriles, such as benzonitrile,

---

[1] Presented in part at the Pacific Conference on Chemistry and Spectroscopy, San Francisco, Calif., Oct 1970.

[2] P. C. Ford, D. F. P. Rudd, R. Gaunder, and H. Taube, *J. Amer. Chem. Soc.*, **90**, 1187 (1968).