$$^{*}K_2 = \frac{[\mathrm{Sc(OH)_2}^{+}][\mathrm{H}^{+}]}{[\mathrm{ScOH}^{2+}]} \tag{17}$$

$$^{\dagger}K_{22} = \frac{[\mathrm{Sc_2(OH)_2}^{4+}]}{[\mathrm{ScOH}^{2+}]^2} \tag{18}$$

$$c_0 = [\mathrm{Sc}^{3+}] + [\mathrm{ScOH}^{2+}] + [\mathrm{Sc(OH)_2}^{+}] + 2[\mathrm{Sc_2(OH)_2}^{4+}] \tag{19}$$

$$\mu = \frac{1}{2}(9[\mathrm{Sc}^{3+}] + 4[\mathrm{ScOH}^{2+}] + [\mathrm{Sc(OH)_2}^{+}] + 16[\mathrm{Sc_2(OH)_2}^{4+}] + [\mathrm{H}^{+}] + 3c_0) \tag{20}$$

$$-\log \gamma_{\mathrm{H}^+} = 0.509\sqrt{\mu} \tag{21}$$

$$[\mathrm{H}^{+}] = \frac{10^{-\mathrm{pH}}}{\gamma_{\mathrm{H}^+}} \tag{22}$$

Using $^{*}K_1 = 10^{-5.1}$, $^{*}K_2 = 10^{-5.1}$, and $^{\dagger}K_{22} = 10^{4.03}$ we find that $\mu = 3.01 \times 10^{-4}\ M$, $[\mathrm{H}^+] = 3.53 \times 10^{-5}\ M$, $[\mathrm{Sc}^{3+}] = 3.99 \times 10^{-5}\ M$, $[\mathrm{ScOH}^{2+}] = 8.97 \times 10^{-6}\ M$, $[\mathrm{Sc(OH)_2}^{+}] = 2.02 \times 10^{-6}\ M$, and $[\mathrm{Sc_2(OH)_2}^{4+}] = 8.57 \times 10^{-7}\ M$. Now suppose we have the unfavorable case in which the ion-recombination rate constants have the plausible, nearly equal values $k_{-1} = 1.0 \times 10^{10}\ M^{-1}\ \mathrm{sec}^{-1}$ and $k_{-3} = 1.7 \times 10^{10}\ M^{-1}\ \mathrm{sec}^{-1}$. From eq 11–15 we would then calculate $\tau_1 = 1.12$ μsec and $\tau_2 = 2.48$ μsec. Two relaxation times differing by even less than the present factor of 2.2 have been reported so our observation of only one τ in the microsecond time range cannot reasonably be ascribed to the two relaxations characterizing this system being too close to one another in time to be resolved.

There is however, another more plausible explanation for observing a single microsecond time range relaxation. The amplitude of one of the two relaxation effects is indetectably small. Thus Hammes and Steinfeld[10] noted that for a coupled system of two equilibria one of the two so-called normal variables y, which are proportional to the amplitudes of the respective signal voltage changes, is a sum of two large terms in the reactant concentrations, specific rates, reciprocal relaxation times, derivatives of the equilibrium constants with respect to the electric field intensity, etc. The other normal concentration variable is a difference of two such terms. It follows that the amplitude of this latter relaxation may be very small. Tentatively accepting this explanation for our E-jump data, we calculate concentrations from eq 16–22 and plot our data first in terms of

$$\tau^{-1} = k_1 + k_{-1}([\mathrm{H}^{+}] + [\mathrm{ScOH}^{2+}]) \tag{23}$$

and then in terms of

$$\tau^{-1} = k_3 + k_{-3}([\mathrm{H}^{+}] + [\mathrm{Sc(OH)_2}^{+}]) \tag{24}$$

Iterating to a constant value of $k_1/k_{-1} = {}^{*}K_1$, the least-squares plot of eq 23 yields $k_1 = 2.9 \times 10^5\ \mathrm{sec}^{-1}$, $k_{-1} = 9.7 \times 10^9\ M^{-1}\ \mathrm{sec}^{-1}$, and $^{*}K_1 = k_1/k_{-1} = 10^{-4.52}$ (titrimetric[12] $^{*}K = 10^{-5.1}$). A similar calculation using eq 24 yields $k_3 = 2.7 \times 10^5\ \mathrm{sec}^{-1}$, $k_{-3} = 1.2 \times 10^{10}\ M^{-1}\ \mathrm{sec}^{-1}$, and $^{*}K_2 = k_3/k^{-3} = 10^{-4.65}$ (titrimetric[12] $^{*}K_2 = 10^{-5.1}$). Evidently it is impossible on the basis of this calculation to say which of the two hydrolysis equilibria, eq 1 and 3, is responsible for the observed E-jump relaxation.

Another explanation for an indetectable second microsecond time range relaxation would be a vanishingly small $\mathrm{Sc(OH)_2}^{+}$ concentration. This suggests a recalculation of specific rates from eq 23 using concentrations calculated from eq 16 and 18–22, deleting terms in $[\mathrm{Sc(OH)_2}^{+}]$ from eq 19 and 20, and using $^{*}K_1 = 10^{-4.61}$ and $^{\dagger}K_{22} = 10^{3.87}$. Iterating to a constant $^{*}K_1$, we obtain from a least-squares plot of τ^{-1} *vs.* $([\mathrm{H}^{+}] + [\mathrm{ScOH}^{2+}])$ the values $k_1 = 1.7 \times 10^5\ \mathrm{sec}^{-1}$, $k_{-1} = 1.0 \times 10^{10}\ M^{-1}\ \mathrm{sec}^{-1}$, and $^{*}K_1 = k_1/k_{-1} = 10^{-4.78}$ (titrimetric[2,11] $^{*}K_1 = 10^{-4.61}$). The agreement of the $^{*}K_1$ values is good. Applying "Occam's razor," the kinetic data of Table I do not require eq 3 for their successful interpretation and the rate constant $k_{-1} = 1 \times 10^{10}\ M^{-1}\ \mathrm{sec}^{-1}$.

From our similar values of k_1 for scandium and aluminum,[18] $k_1 \cong 10^5\ \mathrm{sec}^{-1}$, we predict that a linear relation between k_1 and ionic radius r ranging over many powers of 10 in k_1 for d^0 and d^{10} trivalent metal ions will not be found. Considering the superficial similarity of the splitting off of a proton and of a water molecule from the first coordination sphere of these ions, such a trend in k_1 analogous to that observed[19] for the rate-determining inner coordination sphere water loss in complex ion formation might have been expected.

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Naphthyridine Complexes of Group VIb Metal Carbonyls[1]

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The coordination chemistries of the bidentate nitrogen heterocyclic ligands 1,10-phenanthroline and 2,2′-bipyridine which form five-member chelate ring systems have been extensively studied.[3–5] We wish to report the preparation and characterization of group VIb metal carbonyl complexes with the bidentate nitrogen heterocycle 2,7-dimethyl-1,8-naphthyridine (I). These complexes present a rare example of a four-

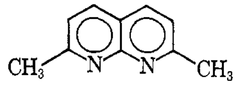

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TABLE I

CO STRETCHING FREQUENCIES AND FORCE CONSTANTS FOR $M(CO)_4L$ MOLECULES

	CO str freq, cm^{-1}				Force constants			Δ(force constants)[a]		
Compound	A_1	B_1	A_1	B_2	k_1	k_2	k_i	Δk_1	Δk_2	pK_a
$Cr(CO)_4(I)$	2016	1905	1884	1836	13.99	15.40	0.37	0.33	0.38	4.50[b]
$Cr(CO)_4(phen)$[c]	2008	1907	1883	1831[d]	13.88	15.37	0.34	0.22	0.35	4.86[d]
$Cr(CO)_4(II)$	2013	1904	1875	1824	13.80	15.38	0.37	0.14	0.36	6.17[e]
$Mo(CO)_4(I)$	2021	1910	1882	1836	13.99	15.48	0.38	0.23	0.22	4.50
$Mo(CO)_4(phen)$	2018	1910	1881	1833	13.93	15.46	0.37	0.17	0.20	4.86
$Mo(CO)_4(II)$	2020	1909	1881	1827	13.86	15.47	0.38	0.10	0.21	6.17
$W(CO)_4(I)$	2012	1897	1875	1831	13.92	15.30	0.38	0.26	0.35	4.50
$W(CO)_4(phen)$	2010	1901	1877	1831[d]	13.90	15.32	0.37	0.24	0.37	4.86
$W(CO)_4(II)$	2010	1895	1873	1824	13.82	15.27	0.38	0.16	0.32	6.17

[a] $\Delta k_n = k_n[M(CO)_4L] - k_n[M(CO)_4(en)]$. [b] T. J. Kress and W. W. Paudler, private communication. [c] phen = 1,10-phenanthroline. [d] Reference 9. [e] A. A. Schilt and G. F. Smith, *J. Phys. Chem.*, **60,** 1546 (1956).

member chelate ring system which is not stabilized by ionic charges and, hence, affords the opportunity to evaluate further the effect of chelate ring size on the bonding in coordination complexes. Since naphthyridine has methyl groups in the 2 and 7 positions, we have also synthesized analogous complexes with 2,9-dimethyl-1,10-phenanthroline (II) for comparison purposes.

Experimental Section

Chromium hexacarbonyl was obtained from Pressure Chemical Co., whereas molybdenum and tungsten hexacarbonyls were generous gifts from Climax Molybdenum Co. 2,9-Dimethyl-1,10-phenanthroline was purchased from G. Frederick Smith Chemical Co. They were all used without further purification. The procedure of Paudler and Kress[6] was used for the preparation of 2,7-dimethyl-1,8-naphthyridine. All solvents were ACS grade which had been dried and stored over molecular sieves and/or sodium. The infrared spectra of the compounds obtained in Nujol–Fluorolube mulls, KBr pellets (4000–600 cm^{-1}), and saturated chloroform solutions (2500–1800 cm^{-1}) were recorded on a Perkin-Elmer Model 621 double-beam grating spectrometer. Polystyrene film was used to provide calibration of all spectra. An authentic sample of $Mo(CO)_4$(1,10-phen) was prepared for spectral comparison purposes.[7] Carbon, hydrogen, and nitrogen compositions were ascertained by combustion.

$Cr(CO)_4(C_{10}H_{10}N_2)$.—A solution of $Cr(CO)_6$ (0.22 g, 1.0 mmol) and $C_{10}H_{10}N_2$ (0.16 g, 1.0 mmol) in 30 ml of *n*-octane was heated at reflux for 4 hr. The solution was cooled in a Dry Ice–acetone bath and filtered. The residue, after washing with methanol followed by petroleum ether (bp 30–60°), provided a dark maroon complex in nearly quantitative yield which exhibits very low solubility in all typical organic media. *Anal.* Calcd for $C_{14}H_{10}N_2O_4Cr$: C, 52.17; H, 3.13; N, 8.69. Found: C, 52.34; H, 3.06; N, 8.78.

$Mo(CO)_4(C_{10}H_{10}N_2)$.—A solution of $Mo(CO)_6$ (0.26 g, 1.0 mmol) and $C_{10}H_{10}N_2$ (0.16 g, 1.0 mmol) in 30 ml of *n*-octane was heated at reflux for 3 hr. Treatment of the solution in a manner analogous to that for $Cr(CO)_4(C_{10}H_{10}N_2)$ gave a deep red product in nearly quantitative yield. *Anal.* Calcd for $C_{14}H_{10}N_2O_4Mo$: C, 45.91; H, 2.75; N, 7.65. Found: C, 46.06; H, 2.91; N, 7.68.

$W(CO)_4(C_{10}H_{10}N_2)$.—A solution of $W(CO)_6$ (0.35 g, 1.0 mmol) and $C_{10}H_{10}N_2$ (0.16 g, 1.0 mmol) in 30 ml of *n*-octane was heated at reflux for 5 hr. Treatment of the solution in a manner analogous to that for $Cr(CO)_4(C_{10}H_{10}N_2)$ gave a dark red complex in nearly quantitative yield. *Anal.* Calcd for $C_{14}H_{10}N_2O_4W$: C, 37.02; H, 2.22; N, 6.17. Found: C, 37.08; H, 2.12; N, 6.21.

$M(CO)_4(C_{14}H_{12}N_2)$ Where M = Cr, Mo, or W.—The 2,9-dimethyl-1,10-phenanthroline complexes were prepared in the same manner as the 2,7-dimethyl-1,8-naphthyridine complexes. *Anal.* Calcd for $Cr(CO)_4(C_{14}H_{12}N_2)$: C, 58.07; H, 3.25; N, 7.52. Found: C, 58.04; H, 3.18; N, 7.65. Calcd for $Mo(CO)_4(C_{14}H_{12}N_2)$: C, 52.06; H, 2.91; N, 6.75. Found: C, 51.64; H, 2.83; N, 6.75. Calcd for $W(CO)_4(C_{14}H_{12}N_2)$: C, 42.88; H, 2.40; N, 5.56. Found: C, 43.10; H, 2.26; N, 5.71.

Results and Discussion

The infrared spectra of the highly colored, air-stable complexes of I and II in the CO stretching region are very similar in number, position, and intensity of absorptions to the spectra of analogous complexes of 2,2′-bipyridine,[8] 1,10-phenanthroline, and its derivatives[9] and therefore are assigned in the same manner. This assignment is confirmed from the force constant calculations of Cotton and Kraihanzel.[10] In Table I are recorded the CO stretching frequencies, force constants, and pK_a values of ligands for selected carbonyl complexes. Infrared absorptions indicative of the ligand moiety in the complexes were observed at approximately 1600, 1500, 1140, 850, 800 and 1590, 1350, 1160, 850, 730 cm^{-1} for ligands I and II, respectively.

Recently Houk and Dobson[11] have presented evidence indicating pyridine and phenanthroline to be of comparable π-bonding ability with bipyridine and pyridine being almost identical. Using the practice of assigning good π-bonding ability to ligands whose carbonyl complexes exhibit high CO force constants,[8,12,13] one would conclude that I is a slightly better π bonder than phenanthroline which in turn is slightly better than II. Apparently the change from a five-member ring chelate to a four-member one does not adversely affect the π-bonding properties of heterocyclic systems.

Cotton and Kraihanzel[8] have argued that π-bonding effects should be evident from the magnitude of the observed change in the k_1 and k_2 force constants relative to a non-π-bonding system such as $M(CO)_4(en)$. Presuming that in the $M(CO)_4L$ complexes the ligand is restricted to the *xy* plane, it may then use the metal d_{xz} and d_{yz} orbitals for π bonding. The CO groups *trans* to the ligand (force constant k_1) may form π interactions with only one of these and the d_{xy} orbital

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while the CO groups *cis* to the ligand (force constant k_2) may interact with both the metal d_{xz} and d_{yz} orbitals. Hence if π bonding with the ligand is involved, k_1 and k_2 should increase and Δk_2 should be approximately $2\Delta k_1$ as is observed for $M(CO)_4(2,2'\text{-bipy})$ compounds.[8] That $\Delta k_1 \cong \Delta k_2$ for $M(CO)_4(py)_2$ was attributed to a nonplanar arrangement of the ligand rings.[8]

From Table I it is found that the complexes $M(CO)_4$-(II) all exhibit $\Delta k_2 \cong 2\Delta k_1$ which by the above argument suggests π interaction. It is surprising to find that $\Delta k_1 \cong \Delta k_2$ for the analogous complexes wherein the ligand is I or phenanthroline. Since these ligands are restricted to a planar configuration, this would appear to imply that neither of them participates appreciably in π bonding in the $M(CO)_4L$ compounds. The inconsistency arising from interpreting both the change in force constant magnitude and the total force constant magnitude to infer π-bonding interaction suggests caution in the use of such arguments.

Several authors[9,14,15] have observed that the position of the CO stretching frequency is directly dependent on the basicity of the ligand and thus have questioned the relation to π-bonding ability. Angelici and Graham[9] reported a linear relation between pK_a and CO stretching frequency for the complexes of the type $M(CO)_4L$ where M = Cr, Mo, or W and L = eight different substituted 1,10-phenanthrolines. From Table I it is found that analogous complexes of II follow very roughly this relationship; however, one finds little correlation when ligands such as I, pyridine,[8,15] and 2,2′-bipyridine[8,16] are considered. Apparently such correlations are extremely dependent on the basic geometry of the ligand system and to a lesser extent on steric factors with respect to coordination.

The two methyl groups of II are found to hinder coordination with transition metal salts.[17,18] If, on coordination to form $M(CO)_4(II)$, there is also a steric problem, such is not in evidence from a comparison of the CO stretching frequencies with less hindered phenanthroline ligands.[9] That the air and thermal stabilities of complexes of I are almost as great as five-member ring chelates and the similar high CO force constants suggests little steric problem due to the two methyl groups.

Preliminary investigations of substitution reactions of $M(CO)_4(I)$ with various monodentate ligands indicate that the reaction rate is similar to that reported for complexes containing five-member chelate rings and thus suggests similar "labilizing" properties.[8,12] Studies of the coordination properties of the naphthyridine ligand system with transition metal salts, metal alkyls, and alkyl halides, as well as other carbonyls, are in progress.

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The Dichromate–Nitrite Reaction in Fused Sodium Nitrite

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In a manner analogous to the behavior of the nitrate ion, the nitrite ion could be expected to act as a Lux base. Attack on Pyrex glass by molten KNO_2 suggests that nitrite is indeed a relatively strong base. Brough, *et al.*,[1] have reported that a brisk reaction occurs when dichromate and nitrite are fused. The reaction

$$Cr_2O_7^{2-} + 2NO_2^- \rightleftharpoons 2CrO_4^{2-} + NO + NO_2 \qquad (1)$$

has been proposed[2] for the reaction of dichromate with nitrite in a sodium nitrate–potassium nitrate eutectic melt, but no accurate determination of the moles of gaseous products produced per mole of dichromate consumed or of the relative proportion of NO to NO_2 in the gaseous products has been made.

Of further interest is the observation that dichromate, a relatively strong oxidizing agent, is not reduced to lower valence chromium species and that in turn nitrite is not oxidized to nitrate (at least directly) by dichromate but undergoes a complex reaction to give NO and NO_2.

This paper is a report of a study to assess the stoichiometry indicated in eq 1 in order to elucidate the basic nature of the nitrite ion.

Experimental Section

Chemicals.—Reagent grade sodium nitrite was recrystallized from aqueous solution and dried under reduced pressure at 130°. Primary standard grade potassium dichromate was used after drying without further purification.

Procedures.—An accurately weighed sample of $K_2Cr_2O_7$ and a large excess of $NaNO_2$ were placed in a reaction vessel of known volume and connected to a mercury manometer and a vacuum manifold. After evacuation, the dichromate–nitrite mixture was fused at about 300°. Gaseous products were rapidly evolved. When the reaction subsided, the melt was allowed to cool and solidify. The reaction vessel was then submerged in a 96° water bath, and the pressure in the reaction vessel was measured. The number of moles of gaseous products was then calculated. The gaseous products were identified from their infrared spectra.

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