$$\mathrm{Co(NH_3)_2{}^{3+}{}_{aq}} \overset{\text{fast}}{\rightleftharpoons} \mathrm{Co(NH_3)_2OH^{2+}{}_{aq} + H^+{}_{aq}} \quad K_\mathrm{h} \tag{3}$$

$$\mathrm{Co(NH_3)_2OH^{2+}{}_{aq} + H_2O_2} \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} \mathrm{Co(NH_3)_2(OH)H_2O_2{}^{2+}{}_{aq}} \tag{4}$$

$$\mathrm{Co(NH_3)_2(OH)H_2O_2{}^{2+}{}_{aq}} \xrightarrow[\mathrm{H^+}]{k_2} \mathrm{Co^{II}{}_{aq} + H_2O_2{\cdot}^+ + 2NH_4{}^+{}_{aq}} \tag{5}$$

$$\mathrm{Co^{III}{}_{aq} + H_2O_2{\cdot}^+} \xrightarrow{\text{fast}} \mathrm{Co^{II}{}_{aq} + 2H^+{}_{aq} + O_2} \tag{6}$$

Reactions 4 and 5 are rate-determining and $H_2O_2{\cdot}^+$ is a radical species.[4] If it is assumed that $K_h/[H^+] \lesssim 0.1$ at the lowest experimental acidity and if the inner-sphere peroxo complex $Co(NH_3)_2(OH)H_2O_2{}^{2+}{}_{aq}$[5] and $H_2O_2{\cdot}^+$ are both in a steady state, then it follows that $K_h \lesssim 5 \times 10^{-3}$ *M* and that

$$k_\mathrm{obsd} = \frac{2k_1k_2K_\mathrm{h}/[\mathrm{H^+}]}{k_{-1} + k_2}[\mathrm{H_2O_2}] \tag{7}$$

A substitution-controlled mechanism corresponds to the situation where $k_2 >> k_{-1}$ in eq 7, in which case $A = 2k_1K_h$ in eq 2, with step 4 forward as the rate-determining step.[1] Substitution of the above upper limit for K_h into the expression for *A* leads to $k_1 \gtrsim 7 \times 10^{-3}$ M^{-1} sec^{-1} at 28.5° and ionic strength 2.0 *M*. Although an acid-independent term cannot be detected, within experimental error, in the empirical rate law for reduction of the aquodiammine by H_2O_2, an upper limit of $k_0 \lesssim 7 \times 10^{-7}$ M^{-1} sec^{-1} at 28.5° is obtained in step 8 if it is assumed that this step makes less than a 10% contribution to the overall rate of reduction at the highest experimental acidity. Comparison of these estimates for k_0 and k_1 indicates

$$\mathrm{Co(NH_3)_2{}^{3+}{}_{aq} + H_2O_2} \xrightarrow[\mathrm{H^+}]{k_0} \mathrm{Co^{II} + H_2O_2{\cdot}^+ + 2NH_4{}^+{}_{aq}} \tag{8}$$

that the presence of inner-sphere OH^- in $Co(NH_3)_2{}^{3+}{}_{aq}$ leads to a ca. 10^4-fold increase in the lability of the remaining water molecules. Similar effects on substitutional lability have been noted in reactions at other aquocobalt(III) centers.[1,2]

Reaction 9 is kinetically indistinguishable from step 4.

$$\mathrm{Co(NH_3)_2{}^{3+}{}_{aq} + HO_2{}^-{}_{aq}} \underset{k_{-1}'}{\overset{k_1'}{\rightleftharpoons}} \mathrm{Co(NH_3)_2HO_2{}^-{}_{aq}} \tag{9}$$

However, the acid dissociation constant of H_2O_2 is $K_a \approx 2 \times 10^{-12}$ *M* at ionic strength 2.0 *M*,[6] and since kinetic indistinguishability leads to $k_1K_h = k_1'K_a$,[4] then $k_1' \approx 4 \times 10^7$ M^{-1} sec^{-1} at 28.5° if reaction 9 is rate determining. Although not entirely ruled out, this alternative rate-determining process seems very unlikely when compared to the data for other reactions of hydrogen peroxide[7] and with the results of Table II.

The narrow range of *A* values and activation parameters for reactions of *cis*-$Co(NH_3)_2OH^{2+}{}_{aq}$ with Cl^-, Br^-, and H_2O_2 strongly suggests that all these processes are controlled by substitution at the Co^{III} center. The acid-independent term observed in the empirical rate law for Br^- oxidation[1] is nonexistent, within experimental error, for reaction with H_2O_2 and Cl^- and the origin of this term remains unclear. It is worth noting that wide and uncertain variations in acid-independent kinetic terms are also a feature of inner-sphere aquocobalt(III) reactions.[2]

Extension of this work to reductants such as SCN^- and thiourea, which have been found to undergo substitution-controlled oxidation by $CoOH^{2+}{}_{aq}$,[2] was found to be impractical because the slow rates of cobalt(III) oxidation of these substrates are similar to those for substrate reaction with the acid perchlorate medium at $[H^+] \gtrsim 0.1$ *M*: kinetic data obtained spectrophotometrically at $[H^+] \gtrsim 0.1$ *M* were too irreproducible to establish the acid dependence of the respective reductions with any certainty with both SCN^- and thiourea as reductants, although a kinetic inverse acid dependence is indicated by initial rate data. The data obtained with $[H^+] = 0.10$ *M* at ionic strength 2 *M* and 25.0° in the reaction with SCN^- (k_obsd = 1.3, 2.8, 3.4$_5$, and 5.1 $\times 10^{-3}$ sec^{-1} at $[SCN^-]$ = 0.10, 0.20, 0.30, and 0.40 *M*, respectively) were sufficiently reproducible to allow comparison with the corresponding data for Br^-, Cl^-, and H_2O_2 oxidations by $Co^{III}(NH_3)_{2aq}$ (ref 1 and this work) under similar experimental conditions. This comparison suggests a substitution-controlled mechanism of oxidation of SCN^- by $Co^{III}(NH_3)_{2aq}$ species.

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Registry No. *cis*-$Co(NH_3)_2{}^{3+}{}_{aq}$, 51262-50-1; H_2O_2, 7722-84-1.

References and Notes

(1) I. Bodek, G. Davies, and J. H. Ferguson, *Inorg. Chem.*, **14**, 1708 (1975).
(2) G. Davies and K. O. Watkins, *J. Phys. Chem.*, **74**, 3388 (1970); G. Davies and B. Warnqvist, *Coord. Chem. Rev.*, **5**, 349 (1970).
(3) R. Bailey and D. F. Boltz, *Anal. Chem.*, **31**, 117 (1959).
(4) G. Davies, *Coord. Chem. Rev.*, **14**, 287 (1974).
(5) The assignment of the inner-sphere complex as $Co(NH_3)_2(OH)H_2O_2{}^{2+}{}_{aq}$ rather than as $Co(NH_3)_2HO_2{}^{2+}{}_{aq}$ is based on a consideration of the relative magnitudes of the acid-dissociation constants of $Co(NH_3)_2{}^{3+}{}_{aq}$ and H_2O_2 (see text). The substitution-controlled mechanism leads, of course, to the same rate-determining step irrespective of this assignment.
(6) M. G. Evans and N. Uri, *Trans. Faraday Soc.*, **45**, 224 (1949).
(7) S. P. Brown, P. Jones, and A. Suggett, *Prog. Inorg. Chem.*, **13**, 205 (1970).

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Nitrogen- and Oxygen-Bonded Nitrosyl. Metal Complexes of the Nitroprusside Ion

AIC50089B

Sir:

The nitrogen atom in (carbon-bound) metal cyanide complexes retains significant Lewis basicity, and as a consequence the cyanide ion is frequently found in a linear-bridged configuration.[1] Similarly, within the past few years the Lewis basicity of oxygen in metal carbonyl complexes has been amply demonstrated.[2] Surprisingly, a bridged configuration for the isoelectronic nitrosyl ligand has never been confirmed, and there are to our knowledge only two claims for such species. Solution infrared studies supported a bridging interaction between π-$CpCr(NO)_2Cl$ and organolanthanides, although no solid species could be obtained,[3] and recently a solid compound

Table I. Infrared Frequencies for $MFe(CN)_5NO$[a]

M	ν_{CN}, cm^{-1}	ν_{NO}, cm^{-1}
Na^+	[2157][b]	1942
Mn^{2+}	2172	1949
Fe^{2+}	2179	1945.5
Co^{2+}	2185	1947
Ni^{2+}	2192	1951
Cu^{2+} form I	2204, 2193 sh	1952
Cu^{2+} form II	2199	1961
Zn^{2+}	2184	1950

[a] Spectra obtained using a Beckman IR-20A spectrometer, with frequency calibration in the cyanide and nitrosyl stretching regions effected using the 2349 cm^{-1} absorption of CO_2 and the 1601.8-cm^{-1} absorption of a polystyrene film. Although for consistency the data reported are specifically for the samples in KBr pellets, the spectra in Nujol mulls are not significantly different. [b] See text for the significance of this value.

Table II. X-Ray Data for $MFe(CN)_5NO$[a]

$CuFe(CN)_5NO$										$MnFe(CN)_5NO$		
Form I			Form II									
	$a = 10.03$ Å $c = 10.88$ Å			$a = 10.05$ Å $c = 10.38$ Å		$a = 10.35$ Å[c] $c = 9.80$ Å		Form III			$a = 16.97$ Å $c = 17.54$ Å	
d_{obsd} (intens)[b]	d_{calcd}	*hkl*	d_{obsd} (intens)	d_{calcd}	*hkl*	d_{calcd}	*hkl*	d_{obsd} (intens)		d_{obsd} (intens)	d_{calcd}	*hkl*
5.437 (s)	5.440	002						5.448 (m)		8.481 (w)	8.485	200
			5.185 (s)	5.190	002	5.175	200	5.180 (w)		7.069 (w)	7.081	112
5.012 (s)	5.015	200						5.021 (s)		5.287 (m)	5.256	113
			4.521 (s)	4.523	201	4.576	201	4.521 (s)		5.136 (s)	5.132	311
3.694 (m)	3.687	202						3.702 (m)		4.943 (m)	4.952	222
			3.610 (m)	3.610	202	3.659	220			4.634 (s)	4.577	312
3.545 (m)	3.546	220						3.557 (m)		4.307 (m)	4.242	400
			3.501 (m)	3.460	003	3.558	202			4.127 (w)	4.124	401
			2.847 (m)	2.850	203	2.932	222	2.843 (w)		3.765 (w)	3.795	420
2.726 (w)	2.720	004						2.735 (w)		3.689 (w)	3.709	421
			2.593 (m)	2.595	004	2.587	400	2.593 (w)		2.833 (m)	2.828	600
2.516 (s)	2.507	400	2.513 (s)	2.512	400	2.502	401	2.515 (s)		2.502 (s)	2.506	007
2.398 (w)	2.391	204								2.450 (w)	2.453	117
2.283 (m)	2.277	402						2.289 (vw)		2.365 (w)	2.360	336
			2.263 (w)	2.261	402	2.252	421			2.308 (w)	2.312	227
2.243 (m)	2.243	420						2.245 (vw)		2.250 (w)	2.240	535
			2.220 (w)	2.196	421	2.214	204					
			2.172 (w)	2.155	332	2.184	332	2.177 (w)				
2.078 (w)	2.080	115										
			1.803 (m)	1.805	404	1.799	441					

[a] Data obtained by film methods using vanadium-filtered chromium radiation. [b] *d* values in angstroms; intensities estimated visually from films. [c] Reference 8.

formed as an intermediate in the reaction of hexacyanoferrate(III) with nitrogen dioxide has been suggested to dimerize through the formation of a linear nitrosyl bridge.[4] We believed that an N- and O-bonded nitrosyl ligand would be accessible if the proper chemical system were selected, and the results which we present here support that belief.

We chose to examine the metal complexes of the nitroprusside ion, on the assumption that the tendency of these systems to attain structures analogous to Prussian Blue[5,6] might force the nitrosyl group to adopt a linearly bridged configuration—i.e., to behave as a "pseudocyanide". The Mn^{2+}, Fe^{2+}, Co^{2+}, Ni^{2+}, Cu^{2+}, and Zn^{2+} salts of $Fe(CN)_5NO^{2-}$ were prepared by direct precipitation from aqueous solution. These materials, which exist as hydrates of the general formulation $MFe(CN)_5NO$, have been characterized previously,[7,8] and only those properties of direct importance to our discussion will be mentioned here. In the course of these investigations it was noted that the Cu complex can be formed in two distinct phases. Although we have not been able consistently to prepare form I, precipitation from acidic solutions appears to yield reasonably pure form II reproducibly.

Infrared Spectra. Table I gives the infrared frequencies of these materials in the cyanide and nitrosyl stretching regions. Sodium nitroprusside actually exhibits four absorptions in the cyanide stretching region, and the value given in Table I, 2157 cm^{-1}, is the weighted average of the infrared-active modes.[8] The metal complexes of nitroprusside exhibit a cyanide absorption at frequencies increased (relative to sodium nitroprusside) by 20–40 cm^{-1}, clearly indicative of the presence of bridging cyanides. The nitrosyl frequencies of the complexes are also increased relative to sodium nitroprusside, and the significance of these values will be discussed later.

X-Ray Powder Patterns. As Inoue et al.[8] have previously shown, the Fe^{2+}, Co^{2+}, Ni^{2+}, and Zn^{2+} salts of nitroprusside adopt the face-centered cubic lattice characteristic of Prussian Blue and its analogs, and our X-ray data are in accord with these results. The reported[8] lattice parameters are as follows: Fe^{2+}, 10.35 Å; Co^{2+}, 10.28 Å; Ni^{2+}, 10.22 Å; Zn^{2+}, 10.36 Å.

The Cu^{2+} complex, however, is not cubic, and we have found that the material as commonly prepared is in fact a mixture of two materials with similar lattice constants. Ayers and Waggoner[7] have reported that this complex crystallizes in a simple-cubic unit cell with a = 7.88 Å. However, the *d* values which Ayers reported elsewhere[9] are clearly incompatible with such a lattice constant. Inoue et al.[8] reported a tetragonal unit cell with a = 10.35 Å and c = 9.80 Å for this material. Although our data support a different assignment for the unit cell, it appears that Inoue has prepared our form II (see below). We have prepared this material more than a dozen times, and in most cases the powder patterns cannot be readily indexed. However, on a few occasions single-phase materials resulted. Table II includes the observed *d* values for the pure forms I and II, as well as the observed powder pattern of a typical two-phase preparation, III. It is clear that III is simply a mixture of forms I and II. (The *d* values reported by Ayers[9] indicate that he has prepared a mixture as well.) Calculated *d* values, as well as *hkl* assignments, are also tabulated for the pure forms. For comparison, calculated *d* values using the unit cell reported by Inoue et al.[8] are also included for form II. On statistical grounds our assignment is favored over that of Inoue et al., and it is also preferable on chemical grounds. It is clear that the structures of copper nitroprusside arise from a tetragonal distortion of the Prussian Blue structure. The structure reported by Inoue et al. would require a rather severe compression along the Fe–CN–Cu bond axis, whereas the structure we propose would require an elongation along the Fe–NO–Cu bond axis. This latter result appears to be in accord with chemical expectations, as well as with recent ESR results[10] which support a distortion along the metal–NO direction. Although there is no obvious reason for the formation of these two similar phases for the same material, this phenomenon of "distortion isomerism" has been observed previously for copper complexes.[11]

The Mn^{2+} complex of nitroprusside is also noncubic, consistent with the noncubic structures observed for several Mn^{2+} complexes of hexacyanometalates.[6] The best fit of our observed *d* values is to a tetragonal unit cell with a = 16.97 Å and c = 17.54 Å, but such values have no obvious structural interpretation. Although our infrared evidence suggests that this material, like the copper complex, is tetragonally elongated along the Fe–NO–Mn axis, the structural ambiguities are such that it will not be discussed further.

Structural Evidence for Bridging Nitrosyl. Both X-ray and infrared evidence support our belief that we have succeeded in forcing the nitrosyl group into a bridged configuration. In the face-centered cubic structure of Prussian Blue and its analogs the Fe–CN–M distance is given by half of the lattice parameter. In the cubic metal nitroprussides this distance also represents the Fe–NO–M distance, and, as Inoue et al. have shown,[8] coupling the known crystal structure of sodium nitroprusside with the observed lattice parameters results in O–M bond distances as follows: Fe^{2+}, 2.42 Å; Co^{2+}, 2.38 Å; Ni^{2+}, 2.35 Å; Zn^{2+}, 2.42 Å. Although Inoue et al. concluded from these distances that an O–M bond does not exist, the O–M interaction must be significant, since the separation is much smaller (0.75 Å) than the sum of the van der Waals radii, estimated as 3.1 Å for Ni–O.[12] The observed Ni–O bond distance of 2.35 Å is nevertheless significantly longer than estimated distances based on ionic, Bragg–Slater, or covalent radii,[12] which are all ca. 2.0 Å. Although the best comparison for bond lengths would be to a crystallographically confirmed N- and O-bonded nitrosyl, a meaningful structural model is available. Duggan and Hendrickson[13] have shown that the di-μ-cyanato-bis(2,2',2''-triaminotriethylamine)dinickel(II) ion is bonded in a dimeric structure via unsupported end-to-end cyanate bridges. Although the observed O–Ni^{2+} distance of 2.34 Å in this complex is longer than expected from either model systems or various radii estimates, both the enforced octahedral geometry and magnetic interactions indicate that there can be no possible ambiguity concerning the existence of an O–Ni^{2+} bond. Since the estimated O–Ni^{2+} distance found in the nitroprusside complex is nearly identical, 2.35 Å, the existence of an O-bonded nitrosyl group is strongly suggested.

Infrared Evidence for Bridging Nitrosyl. If indeed the metal complexes of the nitroprusside ion contain a bridging nitrosyl group, then this bonding should be reflected in the infrared spectrum. We believe that it is but that the relatively small increases observed for the nitrosyl stretching frequency in the cubic complexes are in fact the result of imperfect cancelation of two opposing effects, a conclusion supported by the data for the noncubic copper complex. There is only limited precedent for expectations of change in the nitrosyl stretching frequency upon bridge formation. Since nitrosyl closely resembles carbonyl in its bonding properties, it might reasonably be expected that the shift for nitrosyl, like carbonyl, would be to lower frequencies, and in fact the limited information which is available[3,4] is consistent with this expectation. It is then somewhat surprising that the metal complexes of nitroprusside exhibit an increase in the nitrosyl stretching frequency, but the inability to anticipate such a shift comes from the failure to consider the molecule as a whole, rather than just the perturbations on the nitrosyl fragment. Some years ago, Shriver et al.[14] prepared $Na_2Fe(CNBF_3)_5NO$. As expected, addition of a Lewis acid to the nitrogen end of cyanide produced an increase in CN stretching frequency, from 2157 to 2261 cm^{-1}, consistent with bridge formation. More important, for our purposes, was the observation that the nitrosyl stretching frequency also increased markedly, from 1943 to 2015 cm^{-1}, although there was no direct interaction between the nitrosyl and the BF_3. This relative frequency increase, $\Delta\nu_{CN}/\Delta\nu_{NO} = 1.4$, must be compared to that which we observe for the cubic nitroprusside complexes, $\Delta\nu_{CN}/\Delta\nu_{NO} = 4.5$. The large increase in ν_{NO} for $Na_2Fe(CNBF_3)_5NO$ arises from a change in electron density on iron. When BF_3 is added to cyanide, the electron-acceptor character of the ligand increases, leading to enhanced metal-to-cyanide electron transfer. The resulting decreased electron density on iron leads in turn to decreased iron-to-nitrosyl-π^* π-bonding and consequently to an increased NO bond order and higher stretching frequency. A similar phenomenon is expected to occur in the metal complexes of nitroprusside, but here the Lewis acid is M^{2+}, rather than BF_3. Thus, in the absence of any interaction of the nitrosyl group with M^{2+}, the effect of placing M^{2+} on the cyanide nitrogen atoms should be to increase the nitrosyl frequency, to the extent of perhaps two-thirds of the increase in cyanide frequency, using the BF_3 adduct as a model. In the case of, e.g., the Ni^{2+} complex, the increase in ν_{CN}, 35 cm^{-1}, leads to the expectation of about a 25-cm^{-1} increase in ν_{NO}. The observation that the actual increase, 9 cm^{-1}, is less than half of that expected arises from the fact that the nitrosyl ligand is itself in a bridging configuration which will, as previously discussed, have the effect of reducing the stretching frequency. The actual frequency observed is thus the result of imperfect cancelation of these two opposing effects. The infrared spectra thus support the structural data in providing evidence for the bridging nitrosyl group in the metal complexes of the nitroprusside ion.[15]

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Registry No. $Na_2Fe(CN)_5NO$, 14402-89-2; $MnFe(CN)_5NO$, 25869-27-6; $FeFe(CN)_5NO$, 33751-96-1; $CoFe(CN)_5NO$, 26045-95-4; $NiFe(CN)_5NO$, 14709-61-6; $CuFe(CN)_5NO$, 14709-56-9; $ZnFe(CN)_5NO$, 14709-62-7.

References and Notes

(1) D. F. Shriver, *Struct. Bonding (Berlin)*, **1**, 32 (1966).
(2) D. F. Shriver, *Chem. Br.*, **8**, 419 (1972); A. Alich, N. J. Nelson, D. Strope, and D. F. Shriver, *Inorg. Chem.*, **11**, 2976 (1972).
(3) A. E. Crease and P. Legzdins, *J. Chem. Soc., Dalton Trans.*, 1501 (1973).
(4) J. C. Bates, K. M. Davies, and G. Stedman, *J. Chem. Soc., Dalton Trans.*, 2182 (1974).
(5) J. F. Keggin and F. D. Miles, *Nature (London)*, **137**, 577 (1936).
(6) A. Ludi and H. U. Gudel, *Struct. Bonding (Berlin)*, **14**, 1 (1973).
(7) J. B. Ayers and W. H. Waggoner, *J. Inorg. Nucl. Chem.*, **34**, 2045 (1969).
(8) H. Inoue, H. Iwase, and S. Yanigasawa, *Inorg. Chim. Acta*, **7**, 259 (1973).
(9) J. B. Ayers, Ed.D. Thesis, University of Georgia, 1967.
(10) M. C. R. Symons, D. X. West, and J. G. Wilkinson, *Inorg. Nucl. Chem. Lett.*, **10**, 995 (1974).
(11) J. Gazo, *Pure Appl. Chem.*, **38**, 279 (1974).
(12) J. E. Huheey, "Inorganic Chemistry, Principles of Structure and Reactivity", Harper and Row, New York, N.Y., 1972, p 184.
(13) D. M. Duggan and D. N. Hendrickson, *Inorg. Chem.*, **13**, 2056 (1974).
(14) D. F. Shriver and J. Posner, *J. Am. Chem. Soc.*, **88**, 1672 (1966).
(15) Although for brevity we have chosen not to discuss the infrared spectra of the noncubic complexes, these spectra do support our interpretation of the spectra for the cubic materials.

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