dient tensor. Preliminary measurements of the monocation BFDFe(1+) BF_4 are consistent with this hypothesis. Complete results will be published in a subsequent report.

Acknowledgments. The Francis Bitter National Magnet Laboratory is supported by the National Science Foundation.

References and Notes

(1) Morrison, W. H., Jr.; Hendrickson, D. N. *J. Chem. Phys.* **1973**, *59*, 380.
(2) Cowan, D. O.; Collins, R. L.; Kaufman, F. *J. Phys. Chem.* **1971**, *75*, 2025.
(3) Morrison, W. H., Jr. ; Krogsrud, S.; Hendrickson, D. N, *Inorg. Chem.* **1973**, *12*, 1998.
(4) Cowan, D. O.; Candela, G. A.; Kaufman, F. *J. Am. Chem. Soc.* **1971**, *93*, 3889.
(5) Kaufman, F.; Cowan, D. O. *J. Am. Chem. Soc.* **1970**, *92*, 6198.
(6) Cowan, D. O.; Park, J.; Barber, M.; Swift, P. *Chem. Commun.* **1971**, 1444.
(7) Morrison, W. H., Jr.; Hendrickson, D. N. *Inorg. Chem.* **1975**, *14*, 2331.
(8) LeVanda, C.; Bechgaard, K.; Cowan, D. O.; Mueller-Westerhoff, U. T.; Eilbracht, P.; Candela, G. A.; Collins, R. L. *J. Am. Chem. Soc.* **1976**, *98*, 3181.
(9) Kirchner, R. F.; Loew, G. H.; Mueller-Westerhoff, U. T. *Inorg. Chem.* **1976**, *15*, 2665.
(10) Wertheim, G. K.; Herber, R. H. *J. Chem. Phys.* **1963**, *38*, 2106.
(11) Collins, R. L. *J. Chem. Phys.* **1965**, *42*, 1072.
(12) The experimental spectrum in Figure 3 is a superposition of many spectra corresponding to the various orientations of the principal components of the electric field gradient tensors in the polycrystalline absorber with respect to the external field direction (parallel to the γ-ray propagation direction). The computer simulation mimics this by calculating spectra for discrete orientations and summing with appropriate weighting factors. The solid line in Figure 3 is a composite assuming two sites, with appropriate summation of calculated spectra for each site, and corresponding to the two quadrupole splittings observed in zero field. For a general description of the calculations, see Collins, R. L.; Travis, J. C. "Mössbauer Effect Methodology", I. Gruverman, Ed.; Plenum Press: New York, 1967; Vol. 3, p 123.

Alan W. Rudie, Alan Davison
Department of Chemistry
Massachusetts Institute of Technology
Cambridge, Massachusetts 02139

R. B. Frankel*
Francis Bitter National Magnet Laboratory
Massachusetts Institute of Technology
Cambridge, Massachusetts 02139

Received August 13, 1978

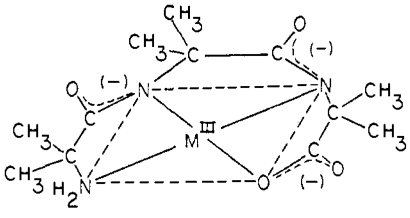
Thermally Stable Copper(III)- and Nickel(III)-Tripeptide Complexes and Their Photochemical Decomposition in Acid Solution

Sir:

Previously, we have reported numerous examples of deprotonated peptide complexes containing copper[1,2] and nickel[3,4] in trivalent oxidation states. These complexes exhibit variable stability in solution, persisting from seconds to hours.[3,5-7] However, both the copper(III) and the nickel(III) complexes undergo self-oxidation-reduction, catalyzed by either acid or base,[6,8,9] in which the ligand is oxidized and the metal ion is reduced. This lack of long-term stability over a wide range of pH often complicates or limits investigations of the reactions of these complexes with other species.

The decomposition products of the copper(III) and nickel(III) complexes of tetraglycine[6,8,9] show that ligand oxidation occurs at the methylene groups. Although tripeptide complexes are in general less stable than tetrapeptide or pentapeptide complexes, studies in this laboratory have shown that the substitution of methyl groups for methylene hydrogens tends to increase the stability of peptide complexes. Thus, copper(III) and nickel(III) complexes of glycylglycylalanine are significantly more stable than their triglycine analogues.

In the present study an amino acid, α-aminoisobutyric acid (Aib), with no methylene hydrogens was used to synthesize the tripeptide and its copper and nickel complexes. Structure I proposed for the $M^{III}(H_{-2}Aib_3)$ complexes is consistent with the structures of many other peptide complexes.[10] Electron spin resonance studies indicate that in solution axial coordination of water molecules occurs with the nickel(III) complex.[7] These complexes of Aib_3 are unusually resistant to decomposition in acid. In the absence of light or reducing agents the copper(III) and nickel(III) complexes show no decomposition over periods of weeks to months in 0.05-0.5 M $HClO_4$. Even in 5 M $HClO_4$ the complexes will last for days to weeks. The inertness of the complexes in acid indicates a remarkable kinetic stability of copper(III) and nickel(III) coordinate bonds toward solvent substitution and an even more remarkable resistance of the peptide coordination to acid attack. In addition the complexes are resistant to self-redox. They are, however, very sensitive to photochemical decomposition by visible radiation. The photolysis causes oxidative decarboxylation of the tripeptide and the formation of acetone.



I

Tri-α-aminoisobutyric acid was prepared by a combination of conventional techniques, starting with the benzyloxycarbonyl amino acid (CbzAib)[11] and the amino acid benzyl ester (AibOBz).[12] Carbodiimide coupling[13] was used to form the dipeptide derivative from these precursors. The dipeptide benzyl ester was formed by reaction of the $CbzAib_2OBz$ with HBr-saturated acetic acid.[14] It was then coupled with another equivalent of CbzAib, again using *N,N′*-dicyclohexylcarbodiimide. The free peptide was isolated by catalytic hydrogenation[13,15] of the Cbz tripeptide benzyl ester. Anal. Calcd for $C_{12}H_{23}N_3O_4$: C, 52.73; H, 8.48; N, 15.37. Found: C, 52.93; H, 8.50; N, 15.34.

Solid samples of $Cu^{III}(H_{-2}Aib_3)$ were prepared by dissolving the pure tripeptide in dilute NaOH, reacting it with freshly precipitated $Cu(OH)_2$, and electrolyzing the copper(II) complex solution by passing it through an electrochemical flow cell.[16] The neutral copper(III) complex was collected in dilute $HClO_4$ in the dark and at low temperatures. Ionic species were separated from this solution by passing it through a Retard-Ion (Bio-Rad) resin. The eluant was then lyophilized, yielding solid $Cu^{III}(H_{-2}Aib_3)$. Anal. Calcd for $CuC_{12}H_{20}N_3O_4$: C, 43.2; H, 6.00; N, 12.6. Found: C, 43.5; H, 6.25; N, 12.5.

A similar procedure was used for $Ni^{III}(H_{-2}Aib_3)$ with special care to avoid basic conditions once nickel(III) was obtained. Anal. Calcd for $NiC_{12}H_{20}N_3O_4$: C, 43.8; H, 6.08; N, 12.8. Found: C, 43.6; H, 6.25; N, 12.9.

Table I outlines some of the properties which characterize the copper(III) and nickel(III) complexes of Aib_3. The ultraviolet-visible (UV-vis) spectra are similar to those of other tripeptide complexes,[4,17] where two intense charge-transfer bands are seen. In general copper(III) has one band at 260-280 and another band with a lower absorptivity at 380-400 nm. Nickel(III) tripeptides typically have bands at 250-260 and 340-360 nm. The reactivity of the Aib_3 complexes with various reducing agents gives further evidence that the trivalent metal complexes are present. Ascorbic acid, hydroquinone, and Fe(II) all react quantitatively with these complexes. This property was utilized in determining their molar absorptivities by spectrophotometric redox titrations.

0002-7863/79/1501-1631$01.00/0

Table I. Properties of the Copper(III)- and Nickel(III)-Aib_3 Complexes

	$Cu^{III}(H_{-2}Aib_3)$	$Ni^{III}(H_{-2}Aib_3)$
UV-vis absorption spectra, λ_{max}, nm (ϵ, $M^{-1} cm^{-1}$)	278 (1.2×10^4) 395 (5.3×10^3)	263 (1.1×10^4) 352 (3.6×10^3)
quantitative reactions with reducing agents (ascorbic acid, hydroquinone, iron(II))	yes	yes
electrode potentials ($M^{III} + e \rightarrow M^{II}$), V	0.66 (vs. NHE)	0.84 (vs. NHE)
electron spin resonance (dilute $HClO_4$, −150 °C, frozen glass)	no signal	$g_x(g_\perp) = 2.258$, $g_y(g_\perp) = 2.312$, $g_z(g_\parallel) = 2.011$, $g_{av} = 2.194$
stability in acid		
0.05 M $HClO_4$	no reaction (16 days) (less 15%, loss in 7 months)	no reaction (12 weeks)
0.5 M $HClO_4$	no reaction (16 days)	
5 M $HClO_4$	30% loss (16 days)	~50% loss (1 day)
photosensitivity, 100-W light (10^{-3} M complex)	complete loss of Cu(III) within 3 min	complete loss of Ni(III) within 30 min
products (% recovd rel to $M^{III}_{initial}$)	Aib_3 (47), acetone (49), CO_2 (53)	Aib_3 (38), acetone (43), CO_2 (40)

The redox potentials of 0.66 and 0.84 V for the copper(III) and nickel(III) complexes, respectively, agree with values predicted from other electrochemical studies.[2,4] In the case of copper, the presence of the six methyl groups in the Aib_3 complex lowers the $E°$ value by 260 mV compared with that of the triglycine (G_3) complex. On the other hand, there is relatively little difference in $E°$ for the Aib_3 and G_3 complexes of nickel.

The presence of trivalent metal is further supported by examination of the ESR spectra. The copper(II) complex loses its ESR signal when oxidized, going from a paramagnetic d^9 system to a low-spin diamagnetic d^8 system. Conversely, diamagnetic d^8 nickel(II)-peptide complexes have no ESR signal until oxidized, giving a paramagnetic, low-spin d^7 complex. The g values for the nickel(III) are characteristic of a tetragonally distorted complex with one unpaired electron in the d_{z^2} orbital.[7] The one carboxylate and three nitrogen donors account for the asymmetry reflected in the $g_\perp$ values.

The stability of these complexes toward substitution, acid attack, and self-redox is remarkable, especially when compared with other metal(III)-tripeptide complexes. The corresponding triglycine complexes decompose completely in minutes under acid conditions,[17,18] whereas $Cu^{III}(H_{-2}Aib_3)$ will not decompose in 0.5 M $HClO_4$ for over 16 days. Even in 5.0 M $HClO_4$ there is only 30% decomposition over the same period. The nickel(III) complex is stable in 0.05 M $HClO_4$ for over 3 months but will decompose completely in a few days in 5 M $HClO_4$. The substitution of methyl groups on the α carbon in the amino acid residues has the desired effect of inhibiting oxidation at that position. Therefore, if oxidation is to occur, it must do so by a less favorable pathway.

The photochemical behavior of these complexes is in some ways as remarkable as their thermal stability. While it is very stable in the dark, the copper(III) complex decomposes completely in <3 min under direct irradiation from a 100-W tungsten lamp. The nickel(III) complex is also light sensitive, but under similar conditions requires ~30 min to decompose. The photodecomposition products in both cases are the divalent metal, carbon dioxide, acetone, and unreacted Aib_3. The acetone and CO_2 are produced in a 1:1 ratio and for copper(III) there is a corresponding loss of Aib_3 which amounts to 50% of that initially present. Chromatographic evidence shows that another species is generated which is presumed to be the dipeptide amide. Equation 1 gives the products for the photocatalyzed decomposition. The $Ni^{III}(H_{-2}Aib_3)$ complex shows a slightly different behavior. Acetone and carbon dioxide are still produced in a 1:1 ratio but more loss of Aib_3 is seen that can be accounted for by carbon dioxide and acetone. This suggests some additional oxidation of the ligand via another mechanism.

$$2Cu^{III}(H_{-2}Aib_3) \xrightarrow[H^+]{h\nu} 2Cu^{II} + H_2Aib_3^+ + HAib_2\text{-amide}^+ + CO_2 + (CH_3)_2CO \quad (1)$$

Photocatalyzed decarboxylations which have been observed in other transition metal aminocarboxylate complexes, such as $Co^{III}(EDTA)$ and $Fe^{III}(HEDTA)OH_2$,[19] $Fe^{III}(NTA)$,[20] and $Co^{III}(Gly)_3$ and $Co^{III}(Ala)_3$,[21] require ultraviolet radiation. However, $Cu^{III}(H_{-2}Aib_3)$ and $Ni^{III}(H_{-2}Aib_3)$ are extremely sensitive to visible as well as ultraviolet radiation. Thus, a quantum yield of 0.18 is found at 468 nm for the copper(III) complex.[22]

The long-term thermal stability of the complexes in acid solution reflects their kinetic inertness to solvent substitution. The rates of dissociation of the Ni(III) and Cu(III) coordinate bonds to nitrogen and oxygen are very sluggish compared with those of the corresponding metal(II) complexes. Normally, strong acid reacts extremely rapidly with the metal-deprotonated peptides,[23-25] but in the present case even 5 M $HClO_4$ is slow to react.

The substitution characteristics of trivalent copper and trivalent nickel complexes have not been explored previously. This work demonstrates the sluggish character of the metal-ligand bond cleavage. The removal of methylene hydrogens from the peptide complexes prevents rapid self-redox reactions in acid and provides a way to isolate crystalline Cu(III) and Ni(III) complexes. Yet the trivalent complexes are very rapid in electron-exchange reactions and are unusually photosensitive.

Acknowledgment. This investigation was supported by Public Health Service Grants No. GM19775 and GM12152 from the National Institutes of General Medical Sciences, and the Purdue Doctoral Fellowship for Black Students (for S. T. Kirksey, Jr.).

References and Notes

(1) Margerum, D. W.; Chellappa, K. L.; Bossu, F. P.; Burce, G. L. *J. Am. Chem. Soc.* **1975**, *97*, 6894.
(2) Bossu, F. P.; Chellappa, K. L.; Margerum, D. W. *J. Am. Chem. Soc.* **1977**, *99*, 2195.
(3) Bossu, F. P.; Margerum, D. W. *J. Am. Chem. Soc.* **1976**, *98*, 4003.
(4) Bossu, F. P.; Margerum, D. W. *Inorg. Chem.* **1977**, *16*, 1210.
(5) Margerum, D. W.; Wong, L. F.; Bossu, F. P.; Chellappa, K. L.; Czarnecki, J. J.; Kirksey, S. T. Jr.; Neubecker, T. A. *Adv. Chem. Ser.* **1977**, No. 162, 281.
(6) Bossu, F. P.; Paniago, E. B.; Margerum, D. W.; Kirksey, S. T. Jr.; Kurtz, J. L. *Inorg. Chem.* **1978**, *17*, 1034.
(7) Lappin, A. G.; Murray, C. K.; Margerum, D. W. *Inorg. Chem.* **1978**, *17*, 1630.
(8) Kurtz, J. L.; Burce, G. L.; Margerum, D. W. *Inorg. Chem.* **1978**, *17*, 2454.
(9) Rybka, J. S.; Kurtz, J. L.; Neubecker, T. A.; Margerum, D. W., unpublished work.
(10) Freeman, H. C.; Schoone, J. C.; Sine, J. G. *Acta Crystallogr.* **1965**, *18*, 381.
(11) Leplawy, M. T.; Jones, D. S.; Kenner, G. W.; Sheppard, R. C. *Tetrahedron* **1960**, *11*, 39.
(12) Zervas, L.; Winitz, M.; Greenstein, J. P. *J. Org. Chem.* **1957**, *22*, 1515.
(13) Greenstein, J. P.; Winitz, M. "Chemistry of the Amino Acids", Wiley: New York, 1961; Vol. 2.
(14) Ben-Ishai, D.; Berger, A. *J. Org. Chem.* **1952**, *17*, 1564.
(15) Shriner, R. L.; Adams, R. *J. Am. Chem. Soc.* **1924**, *46*, 1683.
(16) Blaedel, W. J.; Strohl, J. H. *Anal. Chem.* **1964**, *36*, 1245.
(17) Kurtz, J. L.; Margerum, D. W., unpublished results.

(18) Subak, E. J. Jr.; Loyola, V. M.; Margerum, D. W., unpublished results.
(19) Natarajan, P.; Endicott, J. F. *J. Phys. Chem.* **1973**, *77*, 2049.
(20) Trott, T.; Henwood, R. W.; Langford, C. H. *Environ. Sci. Technol.* **1972**, *6*, 367.
(21) Balzani, V.; Carassiti, V.; Moggi, V.; Sabbatini, N. *Inorg. Chem.* **1965**, *4*, 1247.
(22) Hamburg, A.; Margerum, D. W., unpublished results.
(23) Margerum, D. W.; Dukes, G. R. In "Metal Ions in Biological Systems", Sigel, H., Ed.; Marcel Dekker: New York, 1974; Vol. 1, Chapter 5.
(24) Paniago, E. B.; Margerum, D. W. *J. Am. Chem. Soc.* **1972**, *94*, 6704.
(25) Pagenkopf, G. K.; Margerum, D. W. *J. Am. Chem. Soc.* **1968**, *90*, 501.

Sanford T. Kirksey, Jr., Thomas A. Neubecker
Dale W. Margerum*
Department of Chemistry, Purdue University
West Lafayette, Indiana 47907

Received August 30, 1978

Alane Reduction of Coordinated Carbon Monoxide: Selective Ethene Production

Sir:

With the objective of designing catalyst systems for the selective conversion of synthesis gas, a mixture of carbon monoxide and hydrogen, into added value chemicals, we have examined the stoichiometric reduction of coordinated carbon monoxide using soluble metal complexes. Other workers have demonstrated the reduction of carbon monoxide to give methane,[1,2] mixtures of alkanes,[3,4] methanol,[5] and mixtures of linear alcohols[6] using homogeneous systems. The results presented here, which we believe complement those of Muetteries et al.[3] show that under mild conditions coordinated carbon monoxide can be converted into ethene with >95% selectivity.

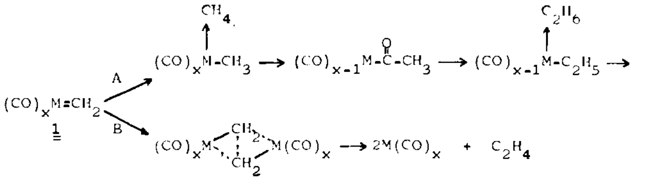
We have previously shown[7] that diborane—a Lewis acid reducing agent—smoothly reduces a coordinated acyl ligand to ethyl probably via initial BH_3 coordination to the acyl oxygen. Since BH_3 proved ineffectual in reducing coordinated carbon monoxide and since, in agreement with other workers,[1,8,9] we believe that dual coordination of CO, i.e., through both the carbon and the oxygen, may well be important in activating it toward reduction, we turned out attention to alane (AlH_3). Compared with BH_3, AlH_3 is both a stronger Lewis acid and a more powerful hydridic reducing agent.

Treatment of $Ru_3(CO)_{12}$ with a 15-fold excess of alane in tetrahydrofuran[10] at 25 °C results in the rapid evolution of methane, ethene, ethane, propene, and propane in the approximate molar ratio 1:1.7:0.5:0.2:0.1.[11] Only ~10% of the CO present in the $Ru_3(CO)_{12}$ is converted into hydrocarbons and further addition of AlH_3/THF has no visible effect. During the reduction no ruthenium metal is formed and the solution remains homogeneous. Attempts to isolate a characterizable ruthenium complex from this solution have been unsuccessful. Addition of 1 M H_2SO_4 to the mixture results in a further gas evolution. This gas contains, in addition to hydrogen resulting from decomposition of excess AlH_x, methane, ethane, and propane in the molar ratio 19:5:1. At this stage conversion of coordinated carbonyl to hydrocarbon products corresponds to ~30%.[12] On addition of the acid the solution turns black and ceases to be homogeneous. With AlD_3, in place of AlH_3, the principal products, before addition of acid are completely deuterated hydrocarbons indicating that the alane is the only source of hydrogen.[13] After addition of the acid 40% of the liberated ethane is $C_2D_4H_2$.

With group 6b metal carbonyl complexes the selectivity to ethene is significantly increased. Thus treatment of $M(CO)_6$, where M = Cr, Mo, or W (0.5 mmol), with AlH_3 (4 mmol) in THF solution at 22 °C results in the selective[14] (95%) formation of ethene. With $Cr(CO)_6$, conversion of carbonyl ligands into ethene increases with increasing AlH_3 concentration reaching a maximum of 17 ± 3% when the $Cr(CO)_6$:AlH_3 molar ratio is 1:6. Further addition of AlH_3 has no effect on the ethene production. Similar results are obtained with $Mo(CO)_6$ and $W(CO)_6$, in that maximum conversion is obtained with a 6 M excess of AlH_3; however the maximum conversion is lower (4% for Mo and 6% for W). With a sixfold excess of AlH_3, ethene evolution is essentially complete within 15 min at 22 °. With AlD_3 in place of AlH_3, C_2D_4 is formed. As was found with $Ru_3(CO)_{12}$, vide supra, acidification of the reaction mixture results in a further gas evolution. Approximately 95% of this gas is hydrogen, derived from the aluminum-hydrido species present in solution; the remaining ~5% consists of methane and ethane in the molar ratio 2;1 for chromium, 10;1 for molybdenum, and 1:5 for tungsten.[15] The *total* conversion of carbonyl ligands into identified[16] organic products, after treatment with AlH_3 followed by acidification, is 33% for $Cr(CO)_6$, 24% for $Mo(CO)_6$, and 25% for $W(CO)_6$[17] indicating that no more than two of the original six carbonyl ligands are converted into identified organic products. We have been unable, as yet, to characterize any inorganic products from these reactions.

Using $LiAlH_4$/THF in place of AlH_3/THF as reducing agent with $Cr(CO)_6$ results in both a reduced conversion (8%) of carbonyl ligands to hydrocarbons and a reduced selectivity (81%) for ethene (the other products being ethane (16%) and propene (3%)).

Although our present data does not permit us to propose detailed mechanisms for these reactions, we feel that the high selectivity to ethene observed strongly suggests the intermediacy of carbenoid metal species. Once formed, such a species, schematically represented as **1**, can be envisaged as either undergoing a reduction-carbonyl insertion-reduction sequence (path A) to give C_1, C_2, and C_3 products or undergoing dimerization (path B) to give ethene. The high selectivity to ethene resulting when path B predominates. Hydrogenation of a carbene fragment and reduction of coordinated acetyl to ethyl, as implicit in path A, have previously been demonstrated[7,18] as has the carbene dimerization[19] implicit in path B.[20] We do not consider that the alternative route to ethene, via β-H elimination from a metal ethyl species, plays a significant role, at least in the $M(CO)_6$/AlH_3 systems, since previous work[7] has shown that decomposition of metal-ethyl species does not generally proceed with such high selectivity to ethene but rather gives a mixture of ethane and ethene.



Primary carbene species have previously been suggested as intermediates in heterogeneous Fischer-Tropsch reactions[21] and dual coordination of carbon monoxide has been suggested to play an important role in activating it toward reduction.[8,9] The present findings add further weight to both of these proposals.

References and Notes

(1) M. G. Thomas, B. F. Beier, and E. L. Muetterties, *J. Am. Chem. Soc.*, **98**, 1296 (1976).
(2) J. C. Huffman, J. G. Stone, W. C. Krusell, and K. G. Caulton, *J. Am. Chem. Soc.*, **99**, 5829 (1977).
(3) G. C. Demitras and E. L. Muetterties, *J. Am. Chem. Soc.*, **99**, 2796 (1977).
(4) J. A. Labinger, K. S. Wang, and W. R. Scheidt, *J. Am. Chem. Soc.*, 100, 3254 (1978).
(5) J. M. Manriguez, D. R. McAlister, R. D. Sanner, and J. E. Bercaw, *J. Am. Chem. Soc.*, **98**, 6733 (1976).
(6) L. I. Shoer and J. Schwartz, *J. Am. Chem. Soc.*, **99**, 5831 (1977).
(7) J. A. van Doorn, C. Masters, and H. C. Volger, *J. Organomet. Chem.*, **105**, 245 (1976).
(8) (a) E. L. Muetterties, *Bull. Soc. Chim. Belg.*, **84**, 959 (1975); (b) *ibid.*, **85**, 451 (1976).

0002-7863/79/1501-1633$01.00/0