Acknowledgment. We gratefully acknowledge financial support of this work from the Science Research Council.

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Received January 19, 1973

The Reductive Degradation of Nitrogen-Containing Ligands in the Presence of Cobalt Ions

Sir:

We have observed the reductive degradation of various cobalt complexes of organic ligands in aqueous borate buffer. Upon reduction by sodium borohydride the complexes break up with deposition, apparently, of metallic cobalt, degradation of the ligand, and evolution of ammonia when the ligand initially contains nitrogen. In at least one system, based on trisodium *meso*-tetra(*p*-sulfonatophenyl)porphinatocobalt(III), $[Co^{III}(tpps)]$, dioxygen significantly affects the course of the degradation and there is a claim that this system reduces dinitrogen to ammonia.[1] Our results are summarized in Table I.

Table I. Degradative Reduction of Cobalt Complexes

System	Yield of ammonia,[a] mol/atom Co
$Na_3[Co^{III}(tpps)]$	0.6
$[Co^{III}(bipy)_3](ClO_4)_3$	0.4
Hexamethyltetraethyltetradehydrocorrin-cobalt(II)	0.5
$[Co^{III}(dmg)_2(H_2O)Cl]$	0.7
$[Co^{II}(o\text{-}NH_2C_6H_4COO)_2]$	0.1
$[Co^{II}(4\text{-}C_5H_4NCOO)_2]$	Nil
$[Co^{III}(acac)_3] + 2\text{-}C_4H_3NHCOOH$	Nil
Dimethylglyoxime (dmg)	Nil
2,2′-Bipyridyl (bipy)	Nil

[a] Borohydride reductions in borate buffer with passage of air at room temperature during 2 days.

We have investigated the reduction of $[Co^{III}(tpps)]$[2] electrochemically, to gain some insight into the route of the degradation. The porphyrin complex was electrolyzed in a three-electrode cell during the passage of purified gas. The gases were purified by acid and alkali scrubbing followed by passage through a trap at −80°. In addition the Ar was passed over hot copper catalyst (Badische Anilin und Soda Fabrik). The working electrode was maintained at a preset potential relative to a saturated calomel electrode within the range −0.5 to −1.5 V. This approximates to the spread of potentials produced by the sodium borohydride during its decomposition in the reaction mixture. Polarography was used to characterize and determine the constituents of the solution (Table II). In addition, the concentrations of free porphyrin (tpps) and $[Co^{III}$-tpps)] were monitored during the reduction by their visible spectra. The cobalt concentration and the ammonia swept out of the system were determined by atomic absorption spectroscopy and by the indophenol test, respectively.

Table II. Polarographic Half-Wave Potentials

	$E_{1/2}$,[a] V		$E_{1/2}$,[a] V
$[Co^{III}(tpps)]$	-0.65[b]	O_2	-0.03
$[Co^{II}(tpps)]$	-1.10[b]	H_2O_2	-0.97
(tpps)	-0.87[b]	Borate buffer (pH 9.7)	-1.9
$(tpps)^-$	-1.63[b]		

[a] Half-wave potentials were measured in borate buffer and are in volts relative to the potassium chloride saturated calomel electrode. [b] The number of electrons involved in the reduction process is assumed to be *one* in agreement with the ratio of wave heights and with published work: H. W. Whitlock and B. K. Bower, *Tetrahedron Lett.*, **32**, 4827 (1965); D. W. Clack and N. S. Hush, *J. Amer. Chem. Soc.*, **87**, 4238 (1965).

Electrolysis at −0.5 V of $[Co^{III}(tpps)]$ in the presence of Ar or air neither produced ammonia nor reduced the complex. However, a reduction at −1.3 V with passage of Ar during 20 hr produced $[Co^{II}(tpps)]$, a 20% decrease in total porphyrin and cobalt concentration, and 0.3 mol of ammonia per atom Co. Under air or $Ar:O_2$ (4:1), the decrease in total porphyrin and cobalt concentrations was now 80%, but the yield of ammonia was 0.2 mol/atom Co. The major product of reduction under these conditions was a reduced nonmetallated derivative of the porphyrin (A) which absorbed at 322 nm and had a $E_{1/2}$ of −1.45 V. The free base (tpps) was also reduced at −1.3 V for 20 hr under both Ar and an $Ar\text{–}O_2$ mixture; however, A was not produced even though there was some degradation of the porphyrin and ammonia was detected (approximately 1 mol/mol porphyrin).

The cobalt(III) porphyrin was also electrolyzed at −1.5 V. Reduction of $[Co^{III}(tpps)]$ with the passage of Ar during 20 hr produced $[Co^{II}(tpps)]$, a 60% decrease in porphyrin and cobalt concentrations, and a negligible amount of NH_3 (0.01 mol/atom Co). When these reductions were carried out both under air or an $Ar\text{–}O_2$ mixture, the final solution did not contain any electroactive species; the degradation of the porphyrin and loss of cobalt from solution were 98% complete, and the yield of NH_3 increased to 0.05 mol/atom Co. During these last electrolyses it was observed that, after the initial 4–5 hr of reduction, another reduced species (B) was formed which, unlike A, did not have a characteristic spectrum but which could be reduced ($E_{1/2}$) at −1.45 V. Species B could not be formed by reducing (tpps) in the presence of $Ar\text{–}O_2$ at −1.5 V. This electrolysis did, however, completely degrade the porphyrin and produced three times more ammonia than the comparable reduction of $[Co^{III}(tpps)]$.

To confirm that A and B are partially reduced porphyrin derivatives, they were prepared by the electrolysis of $[Co^{III}(tpps)]$ under $Ar\text{–}O_2$ mixture at −1.3 and −1.5 V, respectively. Then a second electrolysis was performed with the passage of Ar at −1.5 V which completely reduced A and B and produced ammonia in excess of the amount derived from the reduction of $[Co^{III}(tpps)]$ under Ar at −1.5 V.

The degradation of the porphyrin does not appear to involve removal of cobalt from $[Co^{I}(tpps)]$ by O_2 or a peroxo species, followed by reduction of the free porphyrin, since reduction of (tpps) in the presence of O_2 fails to produce either A or B. Furthermore, since

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(1) E. B. Fleischer and M. Krishnamurthy, *J. Amer. Chem. Soc.*, **94**, 1382 (1972).

(2) Elemental analysis of the cobalt porphyrin indicated that the compound was pure and free from nitrogen-containing impurities.

A and B are different species and are formed during electrolyses which produce markedly different amounts of ammonia, it is suggested that the mechanism of degradation depends on the applied potential, although dioxygen is always involved.

It is possible that some of the ammonia produced in the degradative reduction of $[Co^{III}(tpps)]$ is derived from N_2, as has been claimed.[1] Our results suggest that this is not so. Reduction of $[Co^{III}(tpps)]$ under a 4:1 $(^{15}N)_2:O_2$ mixture produced ammonia with no enrichment of ^{15}N above natural abundance. There was no decrease in ammonia yield when the reduction was carried out under Ar or Ar:O_2 instead of air. We also found that when air scrubbed as described was passed through a solution of borohydride and cobalt tris(acetylacetonate) it yielded 0.1 mol NH_3/atom Co. However, when the air was scrubbed with a solution of cobalt tris(acetylacetonate) and sodium borohydride prior to passage through the other traps and test solution, then no detectable amounts of ammonia were produced. Evidently our air contains nitrogenous impurities which are reducible to ammonia and not easily removed by conventional scrubbing techniques.

We conclude that $[Co^{III}(tpps)]$ does not fix nitrogen under the conditions described[1] and that all the ammonia observed was derived from the combined nitrogen of the ligand.

Acknowledgment. The authors wish to thank Mr. P. E. Meadows for his experimental assistance.

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Received November 10, 1972

Charge Transfer Complexes of Purines and Pyrimidines. 9-Cyclohexyladenine–Iodine in Organic Solvents and in the Solid State

Sir:

The structure and reactivity of nucleic acids is controlled to a large extent by donor–acceptor interactions of the purines and pyrimidines. Yet, in spite of the inherent importance of information about molecular complexes of these compounds, little is known directly about their charge-transfer (CT) interactions. There have been reports that purines and pyrimidines form π complexes with aromatic donors and acceptors such as chloranil, steroids, and the flavines.[1,2] However, weak complexes of these types are undoubtedly stabilized in large part by interactions other than CT forces.[3–5] We report here the first structural and spectral information about a CT complex of a purine which is stabilized primarily by donation of n electrons from a ring nitrogen.

Single crystals of the iodine complex of 9-cyclohexyladenine (CHA) were obtained by allowing iodine to diffuse into a CCl_4 solution of CHA. The unit cell dimensions of the 1:1 complex, $CHA \cdot I_2$, are: $a = 9.1728$ (7), $b = 12.289$ (1), $c = 13.596$ (1) Å; $\beta = 99.564$ (6)°; the space group is $P2_1/c$. A total of 3629 intensity data were used in solving and refining the structure ($R = 0.039$). The iodine forms a CT bond with N(1) of CHA; N(1)···I(1), 2.520 (3) Å and I(1)–I(2), 2.764 (1) Å (Figure 1). Attachment of I_2 at N(1) is an indication that this atom is the most basic ring nitrogen, as is suggested by theoretical charge density calculations[6] and structural observations[7] on protonated adenine derivatives. The CT bond is 0.20–0.25 Å longer than that in the I_2 and ICl complexes of pyridine, 2-picoline, and trimethylamine.[8] The I_2 molecule is not coplanar with the adenine ring, but is inclined to it at an angle of 21.5°. Hydrogen bonding occurs at N(7) and N(10), forming centrosymmetrically related base pairs (Figure 1) of a type not previously observed in crystal structures of self-paired adenine residues. It is interesting to note that this type of pairing has been proposed to account for the stability of the double-stranded helix of polyriboadenylic acid in the low pH range in aqueous media, where N(1) is protonated.[9]

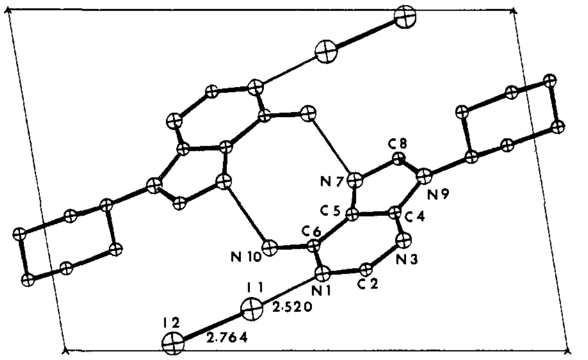

Figure 1. Molecular structure and hydrogen bond pairing in iodine 9-cyclohexyladenine.

The polyiodide solubility method[10] has been used to determine thermodynamic and spectral properties of $CHA \cdot I_2$ in CCl_4. The blue-shifted iodine band of the complex has a maximum absorptivity of 1460 ± 40 l. mol^{-1} cm^{-1} at 415 nm. From measurements of absorbance at the isosbestic point (473 nm) the value of the formation constant (K) is determined to be 186 ± 8 l. mol^{-1}. Spectral properties of the complex are nearly the same in heptane, although owing to the limited solubility of CHA in that solvent, it is difficult to obtain an accurate value of K. A CT band of $CHA \cdot I_2$ is located at 244 nm; it has a peak absorptivity of about 35,000 l. mol^{-1} cm^{-1}. From the frequency of the CT band, an ionization potential of 9.1 eV may be estimated for CHA.[11] All of the spectral and thermodynamic constants determined for $CHA \cdot I_2$ are quite similar to those reported for iodine complexes

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(1) M. A. Slifkin, "Charge-Transfer Interaction of Biomolecules," Academic Press, New York, N. Y., 1971, pp 76–95.

(2) R. Foster, "Organic Charge-Transfer Complexes," Academic Press, New York, N. Y., 1969, pp 350–351.

(3) Reference 2, p 356.

(4) B. L. Van Duuren, *Nature (London)* 210, 622 (1966).

(5) B. Pullman, P. Claverie, and J. Caillet, *Science*, **147**, 1305 (1965).

(6) D. B. Boyd, *J. Amer. Chem. Soc.*, **94**, 64 (1972).

(7) W. Cochran, *Acta Crystallogr.*, **4**, 81 (1951); E. Shefter, M. Barlow, R. Sparks, and K. Trueblood, *J. Amer. Chem. Soc.*, **86**, 1872 (1964); M. Sundaralingam, *Acta Crystallogr.*, **21**, 495 (1966); J. Kraut and L. H. Jensen, *ibid.*, **16**, 79 (1963).

(8) Reference 2, Chapter 8.

(9) A. Rich, D. R. Davies, F. H. C. Crick, and D. J. Watson, *J. Mol. Biol.*, **3**, 71 (1961).

(10) J. D. Childs, S. D. Christian, J. Grundnes, and S. R. Roach, *Acta Chem. Scand.*, **25**, 1679 (1971); J. D. Childs, S. D. Christian, and J. Grundnes, *J. Amer. Chem. Soc.*, **94**, 5657 (1972).

(11) H. Yada, J. Tanaka, and S. Nagakura, *Bull. Chem. Soc. Jap.*, **33**, 1660 (1960); R. S. Mulliken and W. B. Person, *Annu. Rev. Phys. Chem.*, **13**, 107 (1962).