A Linear, Trinuclear, Mixed-Valence Chloro Complex of Ruthenium, $[Ru_3Cl_{12}]^{4-}$

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Abstract: Upon addition of tetraethylammonium chloride to the deep blue solution obtained by dissolving $Ru_2(O_2CCH_3)_4Cl$ in 12 M hydrochloric acid, followed by evaporation in an argon atmosphere, a deep green, crystalline product is isolated. X-ray crystallographic study has defined this substance as $[(C_2H_5)_4N]_2[H_7O_3]_2[Ru_3Cl_{12}]$. The complex anion, which resides on a crystallographic inversion center, may be described as a linear array of three $RuCl_6$ octahedra in which the central one shares two opposite triangular faces with the outer ones. The total of the oxidation numbers of the ruthenium atoms is +8 and from the symmetry it appears that the outer metal atoms are each Ru^{III} and the central one Ru^{II}. The Ru-Ru distances are 2.805 (1) Å and the octahedra are only slightly distorted. The compound crystallizes in space group $P2_1/c$ with unit cell dimensions of $a = 9.542$ (2) Å, $b = 14.940$ (2) Å, $c = 14.403$ (2) Å, $\beta = 104.97$ (1)°, and $V = 1984$ (1) Å^3, with $Z = 2$. With all nonhydrogen atoms treated anisotropically and hydrogen atoms omitted, the structure was refined to $R_1 = 0.050$ and $R_2 = 0.076$. The possible relationship of this anion to the old and still unsolved problem of what complex or complexes are present in solutions of "ruthenium blue" is considered. The existence of bonding interactions between adjacent metal atoms is proposed and discussed.

Introduction

The fact that powerful reductants react with ruthenium in hydrochloric acid solution to form intensely blue solutions has been known for a very long time[1,2] and there have been a number of attempts to identify the complex, or complexes, responsible for the color. The most recent publications are in a state of such flagrant disagreement as to make one wonder if they are dealing with the same problem, although it appears that such is their intention. A paper by Adamson[3] showed that the complex is anionic but also reported a magnetic susceptibility that would apparently require the rather dubious assumption that some of the ruthenium is present as high-spin ruthenium(II). A later paper[4] by the same author suggested specifically that the principal species in 11 M hydrochloric acid is $[RuCl_4]^{2-}$.

Rose and Wilkinson[5] isolated noncrystalline solids for which they proposed formulas containing an anion of composition $[Ru_5Cl_{12}]^{2-}$. They postulated (without any supporting evidence) a "conceivable structure" for this anion in which there is a trigonal bipyramidal cluster of ruthenium atoms without bridging chlorine atoms. The most recent contribution that we have found is a study by Mercer and Dumas,[6] again dealing entirely with species in solution, from which it was concluded that the key species are dinuclear confacial biooctahedral complexes with three μ-chloro ligands, i.e., $[Cl_n(H_2O)_{3-n}Ru(\mu\text{-}Cl)_3RuCl_m(H_2O)_{3-m}]^{-(n+m-2)}$. We thus have schools of thought favoring mononuclear, binuclear, and pentanuclear anionic complexes, and in some cases suggesting structures in considerable detail, but without direct support for any of the often exotic and unprecedented structures.

The work we report here did *not* result from any deliberate effort to solve the "ruthenium blue" problem and we do not, in fact, suggest that we have found a solution to it. We have, however, made some observations that appear likely to be pertinent and we provide, *for the first time* in the entire history of the problem, some firm structural results, obtained by X-ray crystallography; these results agree with *none* of the proposals reviewed above.

We have found that, when we add to a solution of ruthenium blue, prepared by dissolving $Ru_2(O_2CCH_3)_4Cl$ in 12 M HCl, tetraethylammonium chloride and evaporate the solution under argon, a deep green, crystalline solid is obtained. We have, further, shown by X-ray crystallography that this contains a trinuclear anion, $[Ru_3Cl_{12}]^{4-}$. Green precipitates have been mentioned in the past[7,8] but formulas, when assigned, were such as to contain the $[RuCl_4]^{2-}$ ion.

Experimental Section

Preparation. $Ru_2(O_2CCH_3)_4Cl$ (0.03 g), prepared by a literature method,[9] was dissolved in 5 mL of 12 M HCl. The solution was stirred in an argon atmosphere at room temperature. After about 10 min all the solid had dissolved and the color of the solution was deep blue. $(C_2H_5)_4NCl$ (0.03 g) was added and the solution was then evaporated under argon. After 48 h the color of the solution turned green and deep green crystals were formed.

X-ray Crystallography. A crystal of approximate dimensions 0.1 × 0.1 × 0.1 mm was attached to the end of a glass fiber and mounted on a Syntex P$\bar{1}$ four-circle diffractometer. Mo Kα ($\lambda = 0.710\,730$ Å) radiation, with a graphite crystal monochromator in the incident beam, was used.

Rotation photographs and ω scans of several strong reflections indicated that the crystal was of satisfactory quality. Preliminary examination showed that the crystal belonged to the monoclinic system, space group $P2_1/c$. The unit cell dimensions were obtained by a least-square fit of 15 strong reflections in the range $25° < 2\theta < 35°$ giving $a = 9.542$ (2) Å, $b = 14.940$ (2) Å, $c = 14.403$ (2) Å, $\beta = 104.97$ (1)°, and $V = 1984$ (1) Å^3.

Data were measured by θ–2θ scans. A total of 2585 reflections in the range $0° < 2\theta < 45°$ were collected of which 1970 having $I > 3\sigma(I)$ were used to solve and refine the structure. General procedures for data collection have been described elsewhere.[10] The data were corrected for Lorentz and polarization effects. The linear absorption coefficient is 19.4 cm^{-1}; no absorption correction was applied. The heavy-atom positions were obtained from a three-dimensional Patterson function. The structure was refined[11] in space group $P2_1/c$ to convergence using anisotropic thermal parameters for all the nonhydrogen atoms. The discrepancy indices, $R_1 = \Sigma||F_o| - |F_c||/\Sigma|F_o|$ and $R_2 = [\Sigma w(|F_o| - |F_c|)^2/\Sigma w|F_o|^2]^{1/2}$, had final values $R_1 = 0.050$, $R_2 = 0.076$ with a goodness-of-fit parameter equal to 1.66. The final difference map showed no peaks of structural significance. A list of observed and calculated structure factors is available as supplementary material.

Results

The unit cell, which has the symmetry elements of space group $P2_1/c$, contains two of the formula units $[H_7O_3]_2[(C_2H_5)_4N]_2[Ru_3Cl_{12}]$. The four $H_7O_3^+$ ions and the four $(C_2H_5)_4N^+$ ions occupy general positions and have no crystallographically imposed symmetry. The $[Ru_3Cl_{12}]^{4-}$ ions, however reside on crystallographic inversion centers.

The atomic positional and thermal parameters are listed in

0002-7863/80/1502-0608$01.00/0

Table I. Positional and Thermal Parameters and Their Estimated Standard Deviations[a]

atom	*x*	*y*	*z*	*B*(1,1)	*B*(2,2)	*B*(3,3)	*B*(1,2)	*B*(1,3)	*B*(2,3)
Ru(1)	0.030 78(9)	0.072 50(6)	0.183 81(6)	2.51(3)	2.51(4)	1.97(3)	−0.05(3)	0.38(3)	−0.17(3)
Ru(2)	0.000 00(0)	0.000 00(0)	0.000 00(0)	2.49(5)	2.23(5)	1.78(4)	0.08(4)	0.26(4)	0.04(4)
Cl(1)	0.2273(3)	0.0449(2)	0.3197(2)	3.2(1)	3.9(1)	2.7(1)	0.1(1)	0.10(9)	−0.1(1)
Cl(2)	0.1971(3)	0.0898(2)	0.0862(2)	2.9(1)	3.4(1)	2.6(1)	−0.7(1)	0.80(8)	−0.11(9)
Cl(3)	0.0156(3)	−0.0820(2)	0.1440(2)	4.6(1)	2.4(1)	2.1(1)	−0.4(1)	0.26(9)	0.31(9)
Cl(4)	0.0446(4)	0.2272(2)	0.2208(2)	4.9(1)	2.8(1)	4.1(1)	0.5(1)	0.1(1)	−0.7(1)
Cl(5)	−0.1376(3)	0.0495(3)	0.2771(2)	3.5(1)	6.5(2)	3.3(1)	−0.8(1)	1.13(9)	−0.8(1)
Cl(6)	−0.1612(3)	0.1001(2)	0.0447(2)	3.3(1)	4.2(1)	2.6(1)	1.0(1)	0.27(9)	−0.3(1)
Ow(1)	0.172(1)	0.2339(6)	0.4502(6)	5.5(5)	4.4(4)	4.4(4)	−0.6(4)	0.6(4)	0.0(4)
Ow(2)	0.022(1)	0.1006(7)	0.4796(6)	5.0(5)	6.7(5)	4.2(4)	−0.7(4)	0.9(3)	−1.7(4)
Ow(3)	−0.134(1)	0.1274(6)	0.5878(6)	5.1(4)	4.7(5)	5.0(4)	−0.6(4)	2.1(3)	0.7(4)
N	0.501(1)	0.6805(6)	0.7453(6)	2.6(4)	3.4(4)	2.6(3)	0.1(3)	0.5(3)	−0.3(3)
C(1)	0.638(1)	0.645(1)	0.8215(9)	4.0(6)	5.9(7)	4.0(5)	−0.4(6)	1.1(4)	−0.8(6)
C(2)	0.557(2)	0.759(1)	0.6973(10)	5.1(6)	5.1(7)	6.2(6)	−0.1(6)	2.2(5)	2.1(6)
C(3)	0.384(1)	0.711(1)	0.7956(9)	4.5(5)	6.6(8)	4.8(6)	0.6(6)	2.6(4)	−0.7(6)
C(4)	0.433(2)	0.608(1)	0.6767(10)	5.8(7)	5.1(7)	3.8(6)	0.2(6)	0.5(5)	0.4(6)
C(11)	0.605(2)	0.571(1)	0.8838(11)	6.2(8)	5.0(7)	6.0(7)	1.3(7)	1.0(6)	2.1(6)
C(21)	0.424(2)	0.806(1)	0.6192(12)	7.2(9)	6.4(8)	5.4(8)	2.2(8)	0.0(7)	0.6(7)
C(31)	0.441(2)	0.790(1)	0.8636(11)	6.0(7)	7.5(8)	6.5(7)	1.7(7)	2.3(5)	−2.9(6)
C(41)	0.531(2)	0.569(1)	0.6183(11)	9.5(9)	4.6(7)	4.7(6)	2.1(7)	2.1(6)	−1.0(6)

[a] The form of the anisotropic thermal parameter is $\exp[-\frac{1}{4}(B_{11}h^2a^{*2} + B_{22}k^2b^{*2} + B_{33}l^2c^{*2} + 2B_{12}hka^*b^* + 2B_{13}hla^*c^* + 2B_{23}klb^*c^*)]$.

Table II. Bond Distances and Bond Angles for $(H_7O_3^+)_2[(C_2H_5)_4N]_2[Ru_3Cl_{12}]$

atoms	distance	atoms	distance
	Bond Distances (Å)		
Ru(1)-Ru(2)	2.805(1)	Ru(2)-Cl(2)	2.382(2)
-Cl(1)	2.371(1)	-Cl(3)	2.380(2)
-Cl(2)	2.390(1)	-Cl(6)	2.351(2)
-Cl(3)	2.374(1)		
-Cl(4)	2.367(3)	Ow(1)-Ow(2)	2.55(1)
-Cl(5)	2.370(3)	Ow(2)-Ow(3)	2.45(1)
-Cl(6)	2.376(2)		
N-C(1)	1.57(1)	C(1)-C(11)	1.51(2)
-C(2)	1.52(1)	C(2)-C(21)	1.62(2)
-C(3)	1.55(1)	C(3)-C(31)	1.54(2)
-C(4)	1.50(1)	C(4)-C(41)	1.53(2)
	Bond Angles (deg)		
Ru(2)-Ru(1)-Cl(1)	125.41(6)	Ru(1)-Ru(2)-Cl(2)	54.14(5)
-Cl(2)	53.86(5)	-Cl(2)′	125.86(5)
-Cl(3)	53.95(5)	-Cl(3)	53.74(5)
-Cl(4)	125.13(7)	-Cl(3)′	126.26(5)
-Cl(5)	123.91(7)	-Cl(6)	54.02(6)
-Cl(6)	53.2(6)	-Cl(6)′	125.98(6)
Cl(1)-Ru(1)-Cl(2)	90.01(8)	Cl(2)-Ru(2)-Cl(3)	88.41(8)
-Cl(3)	90.93(8)	-Cl(3)′	91.59(8)
-Cl(4)	89.88(9)	-Cl(6)	89.05(8)
-Cl(5)	90.85(9)	-Cl(6)′	90.95(8)
-Cl(6)	178.25(9)	Cl(3)-Ru(2)-Cl(6)	89.26(8)
Cl(2)-Ru(1)-Cl(3)	88.35(8)	-Cl(6)′	90.74(8)
-Cl(4)	91.16(9)		
-Cl(5)	177.53(9)	C(1)-N-C(2)	104.7(8)
-Cl(6)	88.26(8)	-C(3)	110.0(7)
Cl(3)-Ru(1)-Cl(4)	179.05(8)	-C(4)	110.1(8)
Cl(5)	89.32(9)	C(2)-N-C(3)	111.7(8)
-Cl(6)	88.82(8)	-C(4)	113.7(8)
Cl(4)-Ru(1)-Cl(5)	91.16(9)	C(3)-N-C(4)	106.0(8)
-Cl(6)	90.36(9)	Ow(1)-Ow(2)-Ow(3)	115.9(4)
Cl(5)-Ru(1)-Cl(6)	90.88(9)		
Ru(1)-Cl(2)-Ru(2)	72.00(6)	N-C(1)-C(11)	113.8(9)
Ru(1)-Cl(3)-Ru(2)	72.31(6)	-C(2)-C(21)	110.1(9)
Ru(1)-Cl(6)-Ru(2)	72.78(7)	-C(3)-C(31)	110.2(9)
		-C(4)-C(41)	114(1)

Table I. The $[Ru_3Cl_{12}]^{4-}$ ion is depicted in Figure 1. Table II gives the important interatomic distances and angles.

The $H_7O_3^+$ ion is discrete and well defined. It appears to be of the usual type, first described by Williams, Peterson, and Levy[12] and since observed in several other compounds.[13] It can be regarded as a pyramidal H_3O^+ unit to which two additional water molecules are hydrogen bonded. As is typical, the two O-H···O distances are not equal (2.45 (1) and 2.55 (1) Å). The O···O···O angle of 115.9 (4)° is equal to the average of the angles reported[12] for six other examples of $H_7O_3^+$.

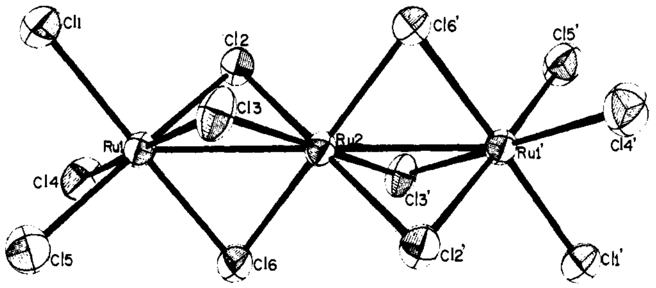

Figure 1. An ORTEP drawing of the $[Ru_3Cl_{12}]^{3-}$ ion. Each atom is represented by its ellipsoid of thermal vibration scaled to give a 40% probability representation of the electron density.

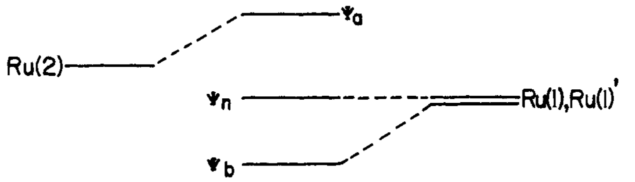

Figure 2. Formation of three-center MOs by interaction of metal d orbitals with lobes along the symmetry axis of the $[Ru_3Cl_{12}]^{4-}$ ion.

The $[(C_2H_5)_4N]^+$ ion is ordered and the observed distances and angles are entirely normal.

The $[Ru_3Cl_{12}]^{4-}$ ion has a very regular, rigorously centrosymmetric structure. Its dimensions correspond very closely to full D_{3d} symmetry. The net charge of 4− requires that there be two Ru^{3+} ions and one Ru^{2+} ion and, barring some rather unlikely disorder, it is reasonable to assume that Ru(1) and Ru(1)′, the outer ruthenium ions, are the trivalent ones. The $Ru^{III}Cl_6$ and $Ru^{II}Cl_6$ moieties should have $t_{2g}{}^5$ and $t_{2g}{}^6$ electron configurations, respectively, and the Ru-Cl distances would therefore be expected to be relatively unaffected by the difference in oxidation number. This is, in fact, the case. The average Ru(2)-Cl distance is 2.371 ± 0.013 Å while the average Ru(1)-Cl distance for the bridging chlorine atoms is 2.380 ± 0.007 Å. The difference is statistically insignificant. It is, perhaps, a bit more surprising that for the terminal $Ru^{III}Cl_6$ octahedra the Ru-Cl bonds to bridging and nonbridging chlorine atoms are also essentially identical, at 2.380 ± 0.007 and 2.369 ± 0.002 Å, respectively.

The various Cl-Ru-Cl angles deviate little from their ideal octahedral values. There is a very slight elongation of the octahedra along the threefold symmetry axis. All of the internal angles, i.e., those such as Cl(2)-Ru(2)-Cl(3), and Cl(2)-Ru(1)-Cl(3) have values slightly below 90°, ranging from 88.26 (8) to 89.26 (8)°, while the others are nearly all slightly greater than 90°, ranging from 89.88 (9) to 91.59 (8)°. The three trans angles about Ru(2) are 180.00° by symmetry while those about Ru(1) deviate slightly from this, having an average value of 178.3 ± 0.3°.

The lack of significant extension or compression of the octahedra along the Ru-Ru-Ru axis suggests that there must be bonding Ru···Ru interactions, since in the absence of any attractive force between the adjacent metal atoms there should be a net repulsion causing an elongation of the octahedra. This point was discussed in considerable detail for confacial bioctahedral structures several years ago by Cotton and Ucko.[14] Thus, for the $[Cr_2Cl_9]^{3-}$ and $[Cr_2Br_9]^{3-}$ structures, where magnetic data show that $t_{2g}{}^3$ configurations are retained on each metal ion with very little interaction, thus ruling out any significant direct Cr-Cr bonding, the bridging $Cr(\mu\text{-}X)_3Cr$ portions of the structure are stretched considerably compared to the ideal value for two fused but undistorted octahedra. Even more pertinent to the present structure are the cases of $[Rh_2Cl_9]^{3-}$ and $[Ru_2Cl_3(Et_2PhP)_6]^+$, where the metal atoms have $t_{2g}{}^6$ configurations: the Cl_{br}-M-Cl_{br} angles are 82.2 and 87.2° while the M-M distances are 3.12 and 3.44 Å, respectively, indicating the extent of stretching that results for a system of confacial octahedra when there is no M-M bonding interaction to offset the repulsive forces between the metal atom cores.

The principal source of attraction between the metal atoms in the $[Ru_3Cl_{12}]^{4-}$ ion can be identified as the formation of three-center MOs by overlap of metal d orbitals having lobes along the threefold symmetry axis. These MOs must have the type of energy distribution shown qualitatively in Figure 2. Since there are only four electrons to occupy these MOs the possible configurations are $\psi_b{}^2\psi_n{}^2$ (low spin) or $\psi_b{}^2\psi_n\psi_a$ (high spin). In either case there is a net bonding interaction. A detailed magnetic investigation is planned for the future to determine which configuration occurs, and, if (as is likely) it is the high-spin configuration, what strength of interelectronic coupling exists.

Discussion

The manner in which the compound reported here is obtained should be fully understood in order that its relationship to the "ruthenium blue" problem be properly appreciated. It is our understanding that the intensely blue solution obtained by dissolving $Ru_2(O_2CCH_3)_4Cl$ in concentrated (12 M) hydrochloric acid contains the authentic "ruthenium blue" species and is essentially similar to the solutions prepared by reduction of ruthenium in higher oxidation states by reducing agents such as zinc. The crystalline compound we have obtained by the procedure described in the Experimental Section is so dark in color that it is impossible to tell with complete certainty whether or not it is blue. However, when it is redissolved in concentrated hydrochloric acid, a solution that is decidedly green is obtained.

We believe that our compound is an oxidation product of the actual "ruthenium blue" species, the oxidation having most likely been caused by oxygen that leaked into the reaction vessel over the long period of evaporation. Rapid concentration of the blue solution gave dark solids that were not crystalline, indicating, perhaps, that the real blue species is reluctant to form crystalline products. On the other hand, deliberate exposure of the solutions to air for long periods of time causes them to become yellow, presumably because all ruthenium atoms in the complex are oxidized to Ru^{III}.

Presumably the real "ruthenium blue" species contains both Ru^{II} and Ru^{III} in a ratio greater than the 1:2 ratio found in our green product. The ratio could be 1:1 as implied by the work of Mercer and Dumas, 2:1 as it would be if the blue species were $[Ru_3Cl_{12}]^{5-}$, that is, the one-electron oxidation product of $[Ru_3Cl_{12}]^{4-}$, or it could be something else not yet considered. The identity of the essential species in "ruthenium blue" remains a matter of speculation at this time.

Whatever the bearing of the $[Ru_3Cl_{12}]^{4-}$ ion on the "ruthenium blue" problem—or even if it has none—it is interesting because it is a type of complex never before reported for ruthenium, nor, so far as we know, for any other metal, with the sole exception of the $[Mo_3Cl_{12}]^{3-}$ ion, for which this type of structure was suggested but not supported with any direct evidence.[15]

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Supplementary Material Available: A table of observed and calculated structure factors (9 pages). Ordering information is given on any current masthead page.

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Cytochrome Oxidase Models. 2. μ-Bipyrimidyl Mixed-Metal Complexes as Synthetic Models for the Fe/Cu Binuclear Active Site of Cytochrome Oxidase[1]

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Abstract: μ-Bipyrimidyl (bipym) mixed-metal complexes, with $[\mathrm{Fe^{II}(bipym)M^{II}}]$ cores ($\mathrm{M^{II}}$ = Cu and Zn), have been synthesized to model the proposed imidazolate-bridged $[\mathrm{Cyt}\ a_3{}^{3+}(\mathrm{imid})\mathrm{Cu_U}{}^{2+}]$ active site structure of cytochrome oxidase where $-J(\mathrm{Fe^{III}}\text{–}\mathrm{Cu^{II}}) \gtrsim 200\ \mathrm{cm^{-1}}$. The binuclear compounds have been prepared from a six-coordinate $[\mathrm{Fe^{II}(C_{18}H_{18}N_6)(bipym)}]^{2+}$ species (B) ($\mathrm{C_{18}H_{18}N_6}$ = a folded macrocycle) by reaction with the appropriate bis(acetylacetonato)M(II) compound in $\mathrm{CH_2Cl_2}$ to yield $[\mathrm{Fe^{II}(C_{18}H_{18}N_6)(bipym)Cu^{II}(acac)_2}]^{2+}$ (C) and $[\mathrm{Fe^{II}(C_{18}H_{18}N_6)(bipym)Zn^{II}(acac)_2}]^{2+}$ (D) as $\mathrm{ClO_4}^-$ salts. Compound B contains low-spin iron(II), whereas C and D are high-spin species in both the solid and solution states at room temperature. Comparative variable-temperature (10–300 K) magnetic susceptibility measurements for C and D indicate C to contain magnetically *isolated* $S = 2$ ($\mathrm{Fe^{II}}$) and $S = 1/2$ ($\mathrm{Cu^{II}}$) centers with $J \approx 0$ through the bipym bridge. The ^{57}Fe Mössbauer spectra of C and D and the $\mathrm{Cu^{II}}$ EPR spectrum of C at 8 K are also supportive of this interpretation. In solution, the redox activity of B, C, and D has been examined by cyclic voltammetry in $\mathrm{CH_2Cl_2}$ where $E_{1/2}$ for the $\mathrm{Fe^{II}/Fe^{III}}$ couple of high-spin C and D are identical at +0.60 V (SCE) and 700 mV lower in potential than for the low-spin monomer compound (B). The $\mathrm{Cu^{II}/Cu^{I}}$ couple for C appears to occur at $E_{1/2} = -0.24$ V (SCE). Finally, the μ-bipyrimidyl $\mathrm{Cu_2}$ compound, $[\mathrm{(hfa)_2Cu^{II}(bipym)Cu^{II}(hfa)_2}]$ ($\mathrm{hfa^-}$ = hexafluoroacetylacetonato anion), has been prepared and found to exhibit an antiferromagnetic exchange interaction with $-J = 7.9\ \mathrm{cm^{-1}}$. The ramifications of these results as they pertain to the magnetically coupled $[\mathrm{Cyt}\ a_3{}^{3+}\text{–}\mathrm{Cu_u}{}^{2+}]$ active site of resting cytochrome oxidase are discussed, and an oxo-bridged alternative to the imidazolate-bridge possibility is also considered in view of the findings from the present model study.

Introduction

One of the most complex and enigmatic of metalloenzymes is cytochrome oxidase, the terminal oxidation/reduction enzyme in mitochondrial respiration. The enzyme catalytically reduces 1 mol of molecular oxygen to 2 mol of water, with the concomitant release of energy which is stored in the ADP–ATP cycle.[4] The protein contains four metal centers (two irons and two coppers) per functioning enzyme unit.[5] Furthermore, through various spectroscopic (EPR, MCD, and UV-vis) and other studies, it is now known that the enzyme contains one isolated iron heme unit (cytochrome *a*) which is low spin in both the oxidized and reduced forms and one isolated copper center ($\mathrm{Cu_D}$; D for EPR detectable), while at the active or oxygen binding site there is a high-spin iron heme (cytochrome a_3) and a second copper center ($\mathrm{Cu_U}$; U for EPR undetectable).[6,7] In a full-temperature magnetochemical study, we have recently shown for the fully oxidized or resting form of the protein that the iron centers of Cyt $a_3{}^{3+}$ and $\mathrm{Cu_U}{}^{2+}$ are strongly coupled antiferromagnetically ($-J \geq 200\ \mathrm{cm^{-1}}$) through a bridge which was suggested to be imidazolate (imid) from a histidine residue.[8,9] This proposed structure for the active site is shown schematically in Figure 1. The observed "strong" magnetic exchange interaction for oxidase is also manifested in the EPR spectrum, where there appears only one $g = 2$ signal which is assigned to magnetically isolated $\mathrm{Cu_D}$ and quantitates to only approximately 40% of the total copper present.[10] This information, in conjunction with the magnetic susceptibility data, appears to rule out any other possible combinations of metal spin-state and exchange interaction as highly unlikely.[8] It does not, however, contribute any information concerning the nature of the possible bridge which mediates the exchange between the iron and copper centers. However, there are two pieces of circumstantial evidence that point to imidazolate as the bridge: (1) EPR measurements indicate that the iron center of the a_3 heme has a nitrogen atom as one of its apical donor atoms[11] and (2) superoxide dismutase, for which a crystal structure is available, contains a mixed-metal binuclear $[\mathrm{Cu^{II}(imid)Zn^{II}}]$ site with an imidazolate bridge from histidine.[12,13]

There are now several examples of synthetic complexes which contain imidazolate-bridged metal centers.[14-18] Thus, there is no question of the bridging capabilities of the imidazolate anion. The controversy that has arisen is over the ability of imidazolate to foster an exchange of the magnitude ($-J \geq 200\ \mathrm{cm^{-1}}$) present for the $[\mathrm{Fe^{III}}\text{–}\mathrm{Cu^{II}}]$ pair of cytochrome oxidase.[8,14,18] For a derivative of superoxide dismutase, with the $\mathrm{Zn^{II}}$ ion replaced by a second $\mathrm{Cu^{II}}$, the strength of the antiferromagnetic exchange between the two $\mathrm{Cu^{II}}$ centers is

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