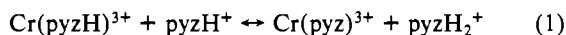


Spectra were recorded with a Nicolet NT-200 WB spectrometer, as previously described.<sup>13,15</sup>

**Results and Discussion.** The <sup>2</sup>H NMR spectra for *cis*- and *trans*-H[Cr(mal)<sub>2</sub>(nic-*N*-2-*d*)<sub>2</sub>], summarized in Table I, show broad resonances centered at -75 and -73 ppm, respectively. Related methylnicotinate and pyridine complexes deuterated at the 2-carbon show similar resonances consistent with the ligand coordination mode assignment (Table I). Carboxyl coordination of nicotinate-2-*d* gives rise to a distinctly narrower resonance centered at ca. +9 ppm (Table I).<sup>2</sup>

Table II summarizes the electronic spectra of *cis*- and *trans*-H[Cr(mal)<sub>2</sub>(nic-*N*)<sub>2</sub>], bands V and IV, respectively. The ligand field spectra are consistent with a Cr(N<sub>2</sub>-O<sub>4</sub>) formulation by comparison with the previously characterized Cr(N<sub>2</sub>-O<sub>4</sub>) complexes listed in Table II. The striking similarity of band maxima and molar absorptivities for band IV and previously characterized *trans*-Li[Cr(mal)<sub>2</sub>(py)<sub>2</sub>]<sup>13</sup> is the basis for the assignment of band IV as *trans*-H[Cr(mal)<sub>2</sub>(nic-*N*)<sub>2</sub>]. Therefore, since band V is also a bis(malonate) bis(nicotinic acid) complex, it must be assigned the *cis* configuration as this is the only other geometrical isomer possible. The larger molar absorptivities for the d-d transitions of this isomer are consistent with the *cis* assignment, due to the lower symmetry associated with the *cis* relative to the *trans* configuration. The geometrical assignments could be made directly from <sup>2</sup>H NMR spectra for the complexes with deuterium-labeled malonate,<sup>13</sup> but so far we have not succeeded in obtaining the desired spectra. Deuteration of the coordinated malonates was carried out as described previously for *trans*-Li[Cr(mal)<sub>2</sub>(py)<sub>2</sub>]<sup>13</sup> and was confirmed by IR spectroscopy. Apparently, the malonate protons (deuterons) undergo facile exchange in solution. This may be due to intramolecular general-base catalysis promoted by the pyridyl carboxyl group, since this facile exchange is not observed in *trans*-Li[Cr(mal)<sub>2</sub>(py)<sub>2</sub>], which was assigned the *trans* configuration by malonate <sup>2</sup>H NMR studies.<sup>13</sup>

Experiments are in progress to determine the mechanism of what appears to be an intriguingly simple reaction. There is little question, though, that nicotinic acid is the oxidant in the reaction. The reduction of nicotinic acid most likely proceeds through a ligand radical ion intermediate,<sup>7</sup> but how the observed chromium(III)-nicotinic acid species are produced is uncertain. Disproportionation of the ligand radical complex or a mechanism similar to the "bleaching reaction" observed by Dunne and Hurst<sup>17</sup> for "pyrazine green", Cr(py<sub>2</sub>H)<sup>3+</sup>, as shown in eq 1 below, are plausible pathways for the production of the observed N-coordinated chromium(III)-nicotinic acid species.



The complexes reported are stable for many hours in aqueous solution at physiological pH, although aquation at the nicotinic acid ligand sites occurs more rapidly on prolonged exposure to light.<sup>18</sup> Thus, if nicotinic acid is essential to the biological role of chromium in glucose metabolism, as has been proposed,<sup>1</sup> the involvement of pyridyl-nitrogen-coordinated nicotinic acid complexes of Cr(III) cannot be ruled out on the basis of instability.

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Department of Chemistry and Program  
in Biochemistry and Biophysics  
Washington State University  
Pullman, Washington 99164-4630

William E. Broderick  
J. Ivan Legg\*

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### Catecholate Coordination to Copper: Structural Characterization of a Tetrachloro-*o*-catecholate-Bridged Dicopper(II) Complex as a Model for Intermediates in Copper-Catalyzed Oxidation of Catechols

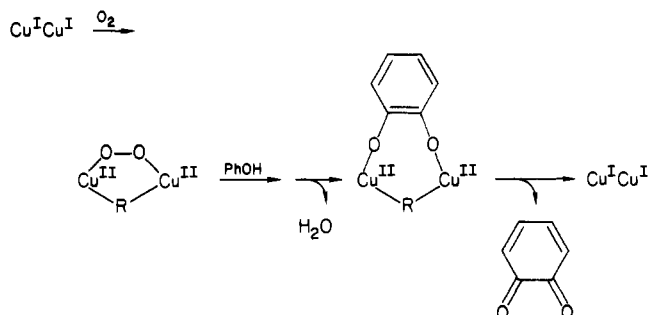
Sir:

Investigations of the interactions and reactivity of catechols, *o*-semiquinones, and *o*-benzoquinones with transition metals have received considerable recent attention.<sup>1-5</sup> Copper-catalyzed oxidative C-C bond cleavage reactions of phenols and catechols have been examined in synthetic procedures,<sup>6</sup> copper(II) catecholate complexes have been studied in model pyrochatechase reactions,<sup>7</sup> and Cu(II)-catecholate and Cu(II)-*o*-semiquinone complexes have recently been studied in connection with the interest in redox chemistry of metal-quinone species.<sup>2-5</sup> Such complexes are also relevant to the two-electron oxidation of catechols to *o*-benzoquinones,<sup>5,6,8,9</sup> which is also an important reaction catalyzed by a binuclear copper ion center in the copper protein tyrosinase.<sup>10</sup> In this protein, it has been proposed<sup>10a,11</sup>

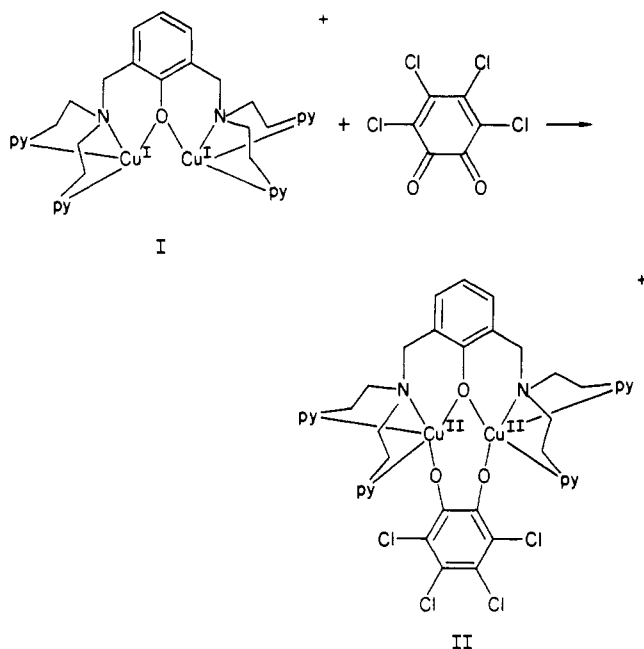
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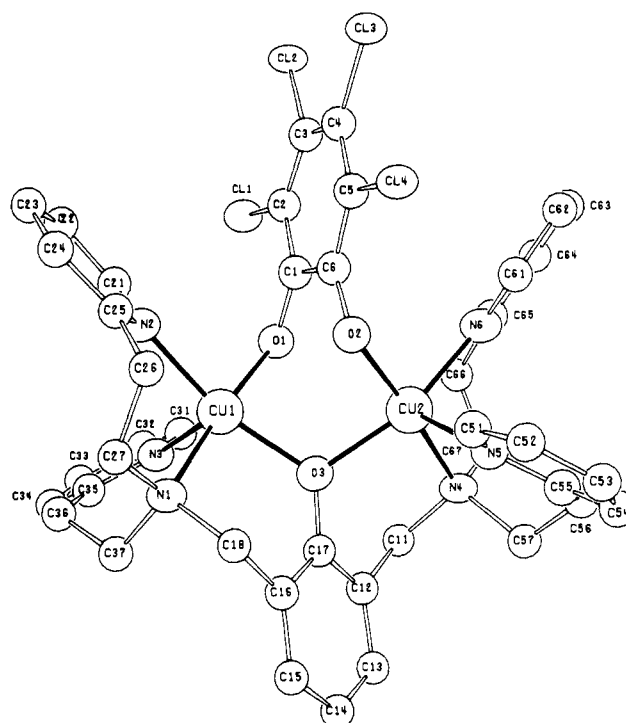
that the interaction of a phenol substrate with a binuclear Cu(II) complex containing a coordinated peroxy ligand (generated from  $2 \text{ Cu(I)} + \text{O}_2$ ) results in the hydroxylation and subsequent coordination of the catecholate dianion to the Cu(II) ions. An intramolecular two-electron-transfer reaction produces the *o*-quinone product and regenerates the binuclear Cu(I) center:



While catecholate coordination to a dicopper(II) center has been proposed in tyrosinase,<sup>10a,11</sup> tyrosinase model systems<sup>6,8,9</sup> and systems catalyzing *o*-catechol C–C bond cleavage reactions,<sup>6,12</sup> structural information on species of this type is lacking. In order to determine the manner in which binding and reactivity may take place in binuclear copper/ $\text{O}_2$ /catechol (and phenol) systems, we are investigating such reactions in well-defined binuclear copper complexes. Here, we report the synthesis and X-ray structural and spectral characterization of a complex containing a catecholate ligand coordinated to and bridging the two Cu(II) ions of a phenoxo-bridged binuclear copper(II) complex. The compound has been synthesized by the "oxidative addition" reaction of tetrachloro-*o*-benzoquinone (TCBQ) with a phenoxo-bridged binuclear Cu(I) complex,  $[\text{Cu}_2(\text{L}-\text{O}^-)]\text{PF}_6$  (I), as shown.



To an orange  $\text{CH}_2\text{Cl}_2$  solution of 0.26 g (0.31 mmol) of I<sup>13</sup> under Ar was added 0.076 g (0.31 mmol) of TCBQ. A dark brown solution immediately formed. The solution was filtered and the product precipitated by adding ether. The solid product was filtered, washed with a  $\text{CH}_2\text{Cl}_2$ /ether (1/2, v/v) mixture, and dried under vacuum, yielding 0.32 g (95%) of the product,  $[\text{Cu}_2(\text{L}-\text{O}^-)(\text{Cl}_4\text{C}_6\text{O}_2)]^+(\text{PF}_6)^-$  (II).<sup>14</sup> Crystals suitable for X-ray



**Figure 1.** ORTEP diagram of the monocation of II, showing the atom-labeling scheme. Selected bond lengths (Å) and angles (deg) are as follows: Cu1...Cu2 = 3.248 (2); Cu1–O1 = 1.995 (9); Cu1–O3 = 1.944 (8); Cu1–N1 = 2.125 (11); Cu1–N2 = 2.040 (10); Cu1–N3 = 2.251 (11); Cu2–O2 = 1.995 (9); Cu2–O3 = 1.943 (8); Cu2–N4 = 2.113 (12); Cu2–N5 = 2.203 (12); Cu2–N6 = 1.995 (10); O1–C1 = 1.330 (16); O2–C6 = 1.314 (15); C1–C6 = 1.381 (19); Cu1–O3–Cu2 = 113.3 (4); O1–Cu1–N1 = 174.9 (4); O1–Cu1–N2 = 92.2 (4); O1–Cu1–N3 = 89.4 (4); O1–Cu1–O3 = 83.7 (4); O3–Cu1–N1 = 91.6 (4); O3–Cu1–N2 = 161.7 (4); O3–Cu1–N3 = 102.3 (4); N1–Cu1–N2 = 91.6 (4); N1–Cu1–N3 = 93.6 (4); N2–Cu1–N3 = 95.5 (4); O2–Cu2–N4 = 175.6 (4); O2–Cu2–N5 = 90.7 (4); O2–Cu2–N6 = 91.9 (4); O2–Cu2–O3 = 85.9 (4); O3–Cu2–N4 = 90.0 (4); O3–Cu2–N5 = 107.8 (4); O3–Cu2–N6 = 158.0 (4); N4–Cu2–N5 = 92.1 (4); N4–Cu2–N6 = 91.3 (5); N5–Cu2–N6 = 94.2 (4).

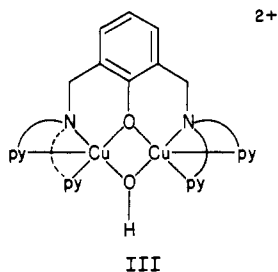
diffraction were obtained by recrystallization from  $\text{CH}_2\text{Cl}_2$ /ether.

The structure of the cation of II is shown in Figure 1.<sup>15,16</sup> The coordination geometry around each Cu(II) center is best described as square-based pyramidal with the amine nitrogen atoms (N1 and N4), one pyridyl nitrogen atom (N2 and N6), the bridging phenoxo oxygen (O3), and one of the catecholate oxygen donors (O1 or O2) forming the basal plane; the second pyridyl nitrogen atom (N3 or N5) occupies the apical position with a longer Cu–N distance, as expected. Each copper ion lies out of the basal plane toward the apical pyridyl nitrogen atom (0.176 Å for Cu1 and 0.209 Å for Cu2). The dihedral angle between the best-fit basal planes for Cu1 and Cu2 is 46.4°. The two Cu(II) basal planes face each other being displaced laterally relative to one another and sharing the bridging phenoxo O3 atom as a common corner. The torsion angle between the vectors defined by the two catecholate oxygen atoms, O1–O2, and Cu1–Cu2 is 63.1°. The Cu(1)···Cu(2) distance of 3.248 (2) Å is expanded, as expected, from the 3.082-Å Cu(II)···Cu(II) distance observed in the closely related phenoxo- and hydroxo-bridged binuclear complex III (where  $\text{OH}^-$  bridges the copper ions instead of catecholate)<sup>17</sup> and

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- (15) The complex II crystallizes in the space group *Pbca* with eight molecules per unit cell:  $a = 18.374$  (3) Å,  $b = 18.346$  (3) Å,  $c = 26.502$  (4) Å,  $\alpha = \beta = \gamma = 90^\circ$ ,  $\rho_{\text{calcd}} = 1.62 \text{ g/cm}^3$ . The positional parameters of the copper atoms were obtained from solutions derived from SHELXL direct-methods software. The remaining non-hydrogen atoms were located in subsequent difference Fourier syntheses. When 2235 unique observed reflections ( $0^\circ < 2\theta < 45^\circ$ ,  $F_o > 6\sigma(F_o)$ ) taken at 22 °C on a Nicolet R3m diffractometer using Mo  $K\alpha$  radiation were used, the structure was refined to current residual values of  $R = 0.064$  and  $R_w = 0.071$ .

- (16) Supplementary material.



is shorter than the 3.6–3.7-Å Cu(I)---Cu(I) distance observed in the precursor complex I. The C1–C6 (1.38 (2) Å) and the C–O (C1–O1 = 1.33 (2) Å, C6–O2 = 1.31 (2) Å) bond lengths of the coordinated  $\text{Cl}_4\text{C}_6\text{O}_2$  ligand indicate that the complete reduction of tetrachloro-*o*-benzoquinone to the coordinated tetrachlorocatecholate (TCC) dianion has occurred, since these bond lengths are diagnostic of the ligand oxidation state (i.e. whether it is coordinated as catecholate, a semiquinone, or a quinone).<sup>1,5,18</sup>

The UV–vis absorption spectrum of II in  $\text{CH}_2\text{Cl}_2$  shows broad peaks with  $\lambda_{\text{max}}$  (nm) ( $\epsilon \text{ M}^{-1} \text{ cm}^{-1}$ ) 640 (1900), 570 (2000), 410 (sh, 3100), and 315 (sh, 9100). The absorption at 410 nm is probably due to a phenoxide to Cu(II) CT transition,<sup>17,19</sup> and the 570-nm band may arise from a catecholate to Cu(II) CT transition by analogy to assignments made for other monomeric Cu(II)–catecholate complexes.<sup>3,7,20</sup> The IR spectrum of II exhibits two strong absorptions at 1260 and 1390  $\text{cm}^{-1}$  where only weak absorptions are observed in the hydroxo-bridged complex, III,<sup>17</sup> thus these bands are assigned to catecholate C–O and ring-stretching vibrations, respectively.<sup>20c</sup>

By contrast to the method of synthesis of complex II, which is stable in the presence of  $\text{O}_2$ , 3,5-di-*tert*-butyl-*o*-benzoquinone (DTBQ) does not react with I. In fact, the “reverse” reaction takes place readily in which 3,5-di-*tert*-butylcatechol (DTBC) is oxidized catalytically to the quinone DTBQ by the binuclear phenoxo- and hydroxo-bridged complex III in the presence of dioxygen.<sup>21</sup> This is therefore a model reaction for the catecholase activity by tyrosinase. In such systems, it is presumed<sup>6,8,9</sup> that a  $\text{Cu}^{\text{II}}_2$ –catecholate complex is formed as an intermediate, which subsequently decomposes to the 1,2-benzoquinone product and a dicopper(I) species. The stability of II to such decomposition reactions is consistent with the higher reduction potential of TCBQ compared to DTBQ.<sup>2</sup> The catecholate complex II thus serves as a structural model for the probable intermediate in the catalytic oxidation of catechols by dicopper moieties and also possibly in copper-catalyzed catechol C–C ring cleavage reactions.<sup>6,7</sup>

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**Supplementary Material Available:** Listings of atomic coordinates and temperature factors, bond lengths, bond angles, and anisotropic temperature factors (12 pages). Ordering information is given on any current masthead page.

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Department of Chemistry  
State University of New York at Albany  
Albany, New York 12222

Kenneth D. Karlin\*  
Yilma Gultneh  
Terrence Nicholson  
Jon Zubieta\*

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## Interlayer Chemistry between Thick Transition-Metal Oxide Layers: Synthesis and Intercalation Reactions of $\text{K}[\text{Ca}_2\text{Na}_{n-3}\text{Nb}_n\text{O}_{3n+1}]$ ( $3 \leq n \leq 7$ )

Sir:

Layered oxides with structures related to perovskite or  $\text{K}_2\text{NiF}_4$  can be generally formulated  $\text{M}_m[\text{A}_{n-1}\text{B}_n\text{O}_{3n+1}]$ , where  $\text{A}_{n-1}\text{B}_n\text{O}_{3n+1}$  is the layer composition and M is an interlayer cation. Each layer has a cubic arrangement of corner-shared  $\text{BO}_6$  octahedra with the large A cations occupying twelve coordinate sites in the center of each cube as found in the perovskite lattice. The layers are formed by limiting the extension of this lattice along one of the three cubic directions. The thickness of each perovskite layer is given then by the value of  $n$  that determines the number of  $\text{BO}_6$  corner-shared octahedra that are connected along a direction perpendicular to the layers. For example, Ruddlesden and Popper described a series of layered alkaline-earth-metal titanates that can be formulated  $\text{Sr}_2[\text{Sr}_{n-1}\text{Ti}_n\text{O}_{3n+1}]$  where  $1 \leq n \leq 3$ .<sup>1</sup> Two of the Sr atoms in each compound occupy nine coordinate sites between the perovskite layers. Most of the phases of this general type that have been reported in the literature<sup>2</sup> contain two M cations ( $m = 2$ ) per formula unit and show no interlayer reaction chemistry. Recently, however, the syntheses and structures of the perovskite layered oxides  $\text{M}\text{Ca}_2\text{Nb}_3\text{O}_{10}$  ( $\text{M} = \text{K}, \text{Rb}, \text{Cs}, \text{Tl}; n = 3; m = 1$ ) have been reported<sup>3</sup> (Figure 1). These new phases, which have a lower layer charge density ( $m = 1$ ), were observed to exchange the interlayer cations in molten lithium, sodium, and ammonium nitrates. The difference in reactivity for ion exchange between the compounds with  $m = 1$  and with  $m = 2$  has an analogy in the 2:1 clay minerals. The smectites have a low interlayer cation density and undergo facile interlayer ion-exchange reactions. In contrast, the micas and vermiculites have a higher interlayer cation density than the smectites and do not readily ion exchange.<sup>4</sup>

We anticipated, by analogy with other layered oxides of comparable layer charge density such as  $\text{KTiNbO}_5$ <sup>5</sup> and  $\text{K}_2\text{Ti}_4\text{O}_9$ ,<sup>6</sup> that ion exchange of  $\text{KCa}_2\text{Nb}_3\text{O}_{10}$  in aqueous acid would lead to the formation of  $\text{H}\text{Ca}_2\text{Nb}_3\text{O}_{10}$  and, further, that chemical substitution should allow for variation of the layer thickness while preserving the chemical reactivity. In this paper we report the synthesis of the series of layered compounds  $\text{K}[\text{Ca}_2\text{Na}_{n-3}\text{Nb}_n\text{O}_{3n+1}]$  by high-temperature reactions of  $\text{KCa}_2\text{Nb}_3\text{O}_{10}$  with  $\text{NaNbO}_3$ . All of the compounds are structurally related to  $\text{KCa}_2\text{Nb}_3\text{O}_{10}$  but differ in the thickness of the perovskite layers. The phases  $\text{K}[\text{Ca}_2\text{Na}_{n-3}\text{Nb}_n\text{O}_{3n+1}]$  readily exchange potassium ions for protons to form  $\text{H}[\text{Ca}_2\text{Na}_{n-3}\text{Nb}_n\text{O}_{3n+1}]$  ( $3 \leq n \leq 7$ ). The compounds formed by this procedure are solid acids and react with organic bases such as primary alkylamines to form intercalated alkylammonium compounds. The intercalation reactions are the first examples of such reactions in perovskite-related layered oxides and are unusual in that they lead to the formation of compounds with thick inorganic layers (up to 27 Å) separated by organic layers in a regular, crystalline manner.

The compound  $\text{KCa}_2\text{Nb}_3\text{O}_{10}$  was prepared at 1200 °C by firing in air  $\text{CaCO}_3$ ,  $\text{K}_2\text{CO}_3$ , and  $\text{Nb}_2\text{O}_5$  mixed in stoichiometric amounts, a procedure similar to that used by Dion et al.<sup>3</sup> The next member of the series  $\text{KCa}_2\text{NaNb}_4\text{O}_{13}$  was prepared similarly by using  $\text{KCa}_2\text{Nb}_3\text{O}_{10}$  and  $\text{NaNbO}_3$  as starting materials. Higher homologues were prepared by reaction of  $\text{KCa}_2\text{NaNb}_4\text{O}_{13}$  with stoichiometric amounts of  $\text{NaNbO}_3$ . Higher reaction tempera-

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