excess of **13**. Subsequent evaporation of the solvents gave a brown solid; UV/Vis (CH_2Cl_2): λ_{max} (%) = 402 (100), 512 (8), 592 nm (5).

7-D_2O and **7**-$H_2{}^{17}O$: To a 10 mM soution of **7**-H_2O (250 μL) in MTHF was added D_2O (100 μL; Cambridge Isotope Laboratories, enrichment of D 99.996%) or $H_2{}^{17}O$ (100 μL; Cambridge Isotope Laboratories, enrichment of ^{17}O 46%), and the mixture was stirred at 25 °C under argon for 12 h. After removal of the water phase the solution was directly used for the EPR experiments.

EPR and ENDOR sample preparation: The solutions of **7**-H_2O, **7**-D_2O, **7**-$H_2{}^{17}O$, and **7**-DIMI in MTHF (Fluka, purum), concentration 5-10 mM, were transferred to an EPR tube and degassed on a vacuum line by the freeze-pump-thaw method.

EPR and ENDOR equipment: The CW EPR spectra at 100 K were recorded on a Bruker ESP 300 spectrometer (microwave frequency 9.485 GHz) with use of a liquid nitrogen cryostat. The CW EPR spectra at 10 K and all pulse EPR and ENDOR spectra (3.3 K throughout) were recorded on a Bruker ESP 380 spectrometer (microwave frequency 9.717 GHz) with use of an Oxford liquid helium cryostat. The CW EPR spectra of frozen solutions were measured with a microwave power of 20 mW, a modulation amplitude of 0.5 mT, and a modulation frequency of 100 kHz. The magnetic field was measured with a Bruker NMR gaussmeter ER 035M. All pulse EPR and ENDOR measurements were conducted at a repetition rate of 1 kHz.

Three-pulse ESEEM spectra:[20] The experiments were carried out with the $\pi/2$-τ-$\pi/2$-t-$\pi/2$-τ-echo pulse sequence, and a pulse length of 16 ns. The echo intensity was measured as a function of time t, which was incremented from 16 to 8200 ns in steps of 8 ns. τ was varied between 88 and 592 ns in steps of 8 ns to avoid signal distortions due to blind spots. Four-step phase cycles were employed to eliminate unwanted echo contributions.[21]

Davies ENDOR spectra:[22] The spectra were recorded with the π-t-$\pi/2$-τ-π-τ-echo pulse sequence, and a pulse length of 48 and 96 ns for the $\pi/2$ and π pulses and a τ value of 104 ns. A selective radio frequency (RF) π pulse of variable frequency ν_{RF} was applied during the time interval t. The length of the RF pulse was 8504 ns, and the RF increment was set to 50 kHz.

Manipulation of EPR and ENDOR data: The data were processed with the program MATLAB 5.1. (The MathWorks, Inc., Natick, MA, USA). The time traces of the three-pulse ESEEM data were baseline corrected with a fifth-degree polynomial function and apodized with a Hamming window. Zero filling was performed prior to Fourier transformation. All frequency domain three-pulse ESEEM results represent absolute-value spectra. To remove blind spots, three-pulse ESEEM spectra measured at different τ values were added together.

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Pyrrole Denitrogenation and Fragmentation of Tetramethylethylenediamine Promoted by a Nb^{II} Cluster**

Maryam Tayebani, Sandro Gambarotta,* and Glenn P. A. Yap

In memory of Lucio Senatore

Metal-promoted cleavage of the C – N bond of amines is a very rare but desirable transformation. So far, this is limited to the cleavage of C – N bonds of strained amines[1] or amidines.[2] Only by using highly reactive trivalent Group 5 metals (Nb and Ta) was it possible to rupture the C – N single bond of aniline[3] and to afford ring-opening of the pyridine aromatic ring.[4] These remarkable reactions are important for the perspectives and the possibilities offered in terms of industrial applications such as denitrogenation[5] of crude oil, catalytic degradation of heterocycles,[6] catalysis, and extrusion of nitrogen and ammonia from organic compounds.[7]

We have recently described the serendipitous preparation and characterization of a Nb^{II} cluster $[(tmeda)_2Nb_2Cl_5Li-$

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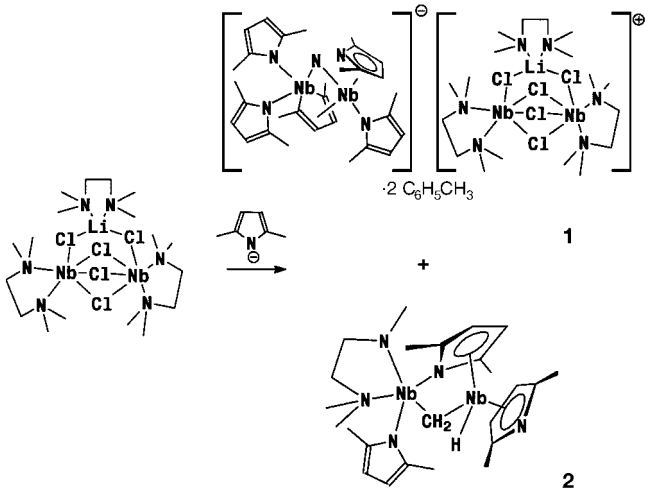
(tmeda)][8a] and reported how this species, upon ligand replacement by anionic amides, performs C–N, N–N, and C–H bond cleavage.[8] Herein we describe the first nitrogen atom abstraction from a pyrrole ring and fragmentation of a neutral tertiary amine.

In a complex redox reaction, the divalent complex $[(tmeda)_2Nb_2Cl_5Li(tmeda)]$[8a] reacts rapidly with the dimethylpyrrole lithium salt 2,5-$Me_2C_4H_2NLi$ in THF to afford a mixture of ionic **1** and neutral **2** (Scheme 1). Both compounds were isolated in analytically pure form by fractional crystallization and their structures were elucidated by X-ray diffraction.



Scheme 1. Synthesis of **1** and **2**.

The unit cell of **1** contains two units in the ratio 1:1. The cation $[(tmeda)_2Nb_2Cl_5Li(tmeda)]^+$, which contains both di- and trivalent niobium centers, displays isostructural connectivity with the divalent starting material $[(tmeda)_2Nb_2Cl_5Li(tmeda)]$ but with significantly different bond lengths and angles: the Nb–Nb distance (Nb(3)–Nb(4) 2.5211(6) Å) in **1** is considerably longer than in the neutral Nb^{II} starting complex (Nb–Nb 2.400(2) Å)[8a] and closely resembles that of the neutral mixed-valence ($Nb^{II}Nb^{III}$) complex $[(tmeda)_2Nb_2Cl_5]$ (Nb–Nb 2.545(1) Å) previously described.[8c] The anion of **1** is formed by two tetravalent niobium atoms (or one tri- and one pentavalent niobium atoms; Figure 1) linked together by one bridging nitride and one bridging dienediyl moiety, both of which arise from dimethylpyrrole denitrogenation. This moiety is σ-bonded to the Nb(1) metal center through the two terminal carbon atoms thus forming a planar niobacyclopentadiene ring, and is also symmetrically π-bonded to the second metal center.

The structural data clearly indicate that the cation of **1** is a mixed-valence $Nb^{II}Nb^{III}$ species, and is thus paramagnetic. Conversely, the anion is probably diamagnetic. The magnetic moment of **1** ($\mu_{eff} = 1.76\ \mu_B$ per formula) is indicative of the presence of only one unpaired electron per formula unit. Furthermore, the paramagnetic mixed-valence compound $[(tmeda)_2Nb_2Cl_5]$ was obtained as an insoluble, paramagnetic purple solid[8c] by treatment of crystalline **1** with THF. A diamagnetic solution remained whose NMR spectra were

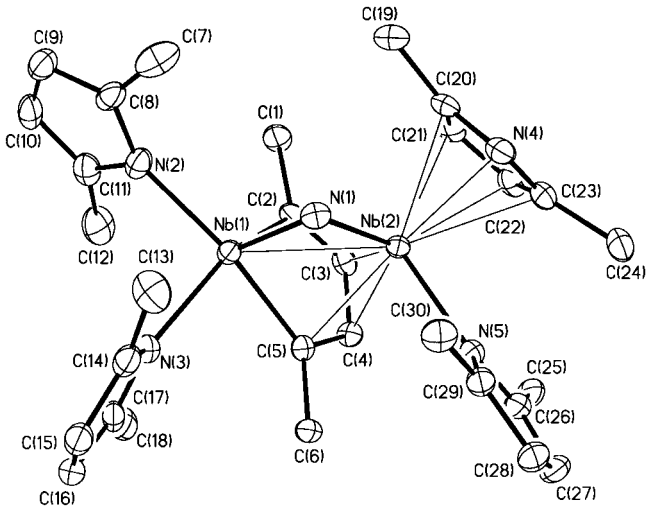


Figure 1. ORTEP drawing of the anion of **1**. Thermal ellipsoids are drawn at the 30% probability level. Selected bond lengths [Å] and torsion angles [°]: Nb(1)–N(1) 1.857(3), Nb(2)–N(1) 1.948(3), Nb(1)–C(2) 2.162(4), Nb(1)–C(5) 2.166(4), Nb(2)–C(2) 2.423(4), Nb(2)–C(3) 2.379(4), Nb(2)–C(4) 2.378(4), Nb(2)–C(5) 2.390(4), Nb(1)–N(2) 2.166(3), Nb(1)–N(3) 2.154(3), Nb(2)–N(4) 2.483(4), Nb(2)–C(20) 2.468(4), Nb(2)–C(21) 2.437(4), Nb(2)–C(23) 2.519(4); Nb(1)-C(2)-C(3)-C(4) 5.5(2), Nb(1)-C(5)-C(4)-C(3) 2.6(2), Nb(1)-N(2)-C(8)-C(9) 193.2(2).

consistent with the formulation $[\{(2,5\text{-}Me_2C_4H_2N)_2Nb\}\{(\eta^5\text{-}2,5\text{-}Me_2C_4H_2N)(2,5\text{-}Me_2C_4H_2N)Nb\}(\mu\text{-}N)(\mu,\eta':\eta':\eta^4\text{-}1,4\text{-}Me_2C_4H_2)][Li(tmeda)_2]$. The diamagnetism of this anion may be explained with the presence of a Nb–Nb single bond which is in agreement with the fairly short Nb–Nb distance (Nb(1)–Nb(2) 2.7872(7) Å).

The dinulcear complex **2** has two inequivalent niobium atoms. The Nb(2) center is π-bonded to two pyrrolyl rings forming a bent metallocene-like structure (Figure 2). One of the two pyrrolyl rings is also σ-bonded to the Nb(1) center

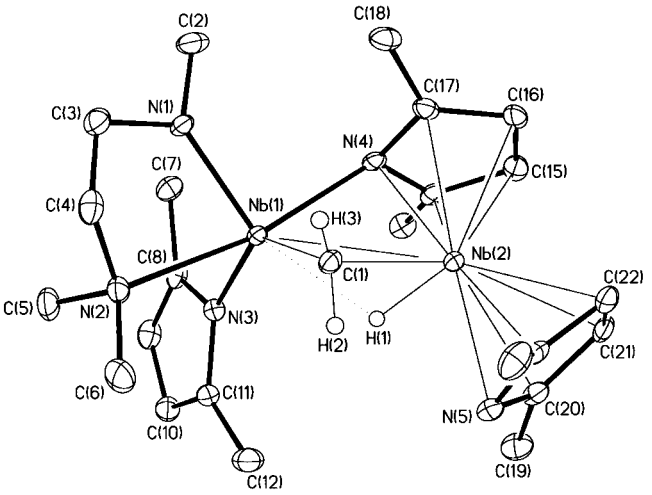


Figure 2. ORTEP drawing of **2**. Thermal ellipsoids are drawn at the 30% probability level. Selected bond lengths [Å] and angles [°]: Nb(2)–N(4) 2.201(3), Nb(2)–C(17) 2.319(4), Nb(2)–C(16) 2.417(4), Nb(2)–N(5) 2.341(3), Nb(2)–C(20) 2.355(4), Nb(2)–C(21) 2.442(4), Nb(1)–N(2) 2.404(4), Nb(1)–N(1) 2.004(3), Nb(1)–N(3) 2.172(3), Nb(1)–N(4) 2.201(3), Nb(1)–C(1) 2.098(4), Nb(2)–C(1) 2.272(4); Nb(1)-C(1)-Nb(2) 85.7(2), $C_4N_{centroid}$-Nb(2)-$C_4N_{centroid}$ 136.6(2).

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which, in turn, is σ-bonded to another pyrrolyl ring and to one demethylated tmeda molecule. One bridging methylene group (Nb(1)–C(1) 2.098(4), Nb(2)–C(1) 2.272(4) Å) and one hydride atom (Nb(1)–H(1) 2.270(6), Nb(2)–H(1) 1.708(6) Å) are asymmetrically placed between the two metal centers and complete the structure. The crystal structure was of sufficient quality to locate and refine the hydride center and the methylene hydrogen atom positions.

Complex **2** is a paramagnetic mixed-valence $Nb^{III}Nb^{IV}$ species and its magnetic moment is consistent with the presence of one unpaired electron per formula unit ($\mu_{eff} = 1.77\ \mu_B$ per formula). In this case it was not possible to obtain satisfactory NMR data to support the proposed formulation. However, chemical degradation experiments carried out with anhydrous HCl in a closed vessel connected with a Toepler pump yielded 64% of the expected amount of H_2 and CH_4. The presence of a medium intensity resonance at 1637 cm^{-1} in the IR spectrum (Nb–H stretching) suggests that complex **2** should be regarded as a terminal rather than bridging hydride species. Unfortunately, isotope exchange experiments with D_2 failed due to the fact that the complex reacts in a destructive manner with hydrogen gas. In spite of the paramagnetism, reproducible ^1H NMR spectra show the resonances of two pyrrolyl rings as sharp, well resolved peaks. Also two rather broad features possibly account for the presence of the hydride ($\delta = 4.91$) and the methylene group ($\delta = 9.22$), as they have the correct integration. Conversely, no resonances were conclusively identified for the demethylated tmeda molecule. Perhaps, the partially resolved spectrum may be ascribed to either the 18 electron configuration of the niobium atom π-bonded to two pyrrolyl rings, or to possible dissociation of the dimeric structure in solution.

The formation of **1** and **2** arises from two different processes within the same reaction. Complex **1** is clearly the result of the cooperative attack of the two Nb^{II} centers on one pyrrolyl anion. The four electrons necessary to form the nitride and the dienyl dianion are obtained from the five electrons provided by the oxidation of the four Nb^{II} centers during the formation of **1**. The formation of **2** arises instead from the cleavage of one CH_3–N bond of the tmeda molecule and subsequent oxidative addition into the C–H bond of the cleaved CH_3 group. This process also requires four electrons. However, complex **2** is a mixed-valence $Nb^{III}Nb^{IV}$ complex and thus only three electrons were obtained from the two metal centers. Therefore, the formation of the two complexes appears to be interconnected in the sense that the total of eight electrons necessary for the pyrrole denitrogenation and tmeda fragmentation are provided by the formal oxidation of five niobium atoms leading to the formation of three Nb^{IV} and two Nb^{III} centers. A sixth Nb^{II} atom conserved the original divalent state and formed with one of the two Nb^{III} centers the mixed-valence Nb^{II}/Nb^{III} cation of **1**.

Experimental Section

Solid $[Nb_2Cl_5Li(tmeda)_3]$ (2.0 g, 2.8 mmol) was added to a solution of the lithium salt of 2,5-dimethylpyrrole (1.1 g, 11.0 mmol) in THF (100 mL) at room temperature. The mixture was evaporated to dryness and the residual solid was redissolved in toluene (70 mL). After filtration, diethyl ether (30 mL) was added, and the mixture was left to stand at −30 °C. This afforded dark crystals of **1** (0.2 g, 0.13 mmol, 14%). Elemental analysis (%) calcd for $C_{62}H_{105}N_{11}Nb_4LiCl_5$: C 47.72, H 6.78, N 9.87; found C 47.66, H 6.43, N 9.27; IR (Nujol mull): $\tilde{\nu} = 1495$ (w), 1376 (s), 1290 (w), 1255 (m), 1242 (m), 1233 (m), 1059 (s), 1036 (m), 1011 (m), 949 (m), 916 (w), 792 (s), 763 (m), 743 (m), 729 (s), 697 (w), 578 (m) cm^{-1}; magnetic moment: $\mu_{eff} = 1.76\ \mu_B$. ^1H NMR (500 MHz, C_6D_6, 23 °C, the tube was centrifuged to remove the purple insoluble $[Nb_2Cl_5(tmeda)_2]$: $\delta = 7.13$ (m, 10H, toluene), 5.88 (s, 2H, diene), 5.44 (s, 4H, pyrrole), 5.41 (s, 4H, pyrrole), 2.64 (s, 6H, Me-pyrrole), 2.49 (s, 6H, Me-pyrrole), 2.30 (s, 8H, CH_2-tmeda), 2.15 (s, 24H, Me-tmeda), 2.12 (s, 6H, toluene), 2.08 (br. s, 12H, Me-pyrrole), 0.88 (s, 6H, Me-diene); ^{13}C NMR (127.7 MHz, C_6D_6, 23 °C): $\delta = 139.2$(C_q-diene), 138.4, 135.3, 132.3 (C_q-pyrrole), 128.7, 128.9, 126.0 (toluene), 115.9 (CH-diene), 107.6, 107.0 (CH-pyrrole), 58.9 (CH_2-tmeda), 46.2 (Me-tmeda), 29.2 (Me-diene), 21.4, 18.5, 18.4, 17.5 (Me-pyrrole), 13.0 (Me-toluene).

The mother liquor of the above preparation was evaporated to dryness. The solid residue was redissolved in diethyl ether (100 mL), quickly filtered, and allowed to stand undisturbed at room temperature for a few hours. Dark green crystals of **2** separated (0.05 g, 0.08 mmol, 9%). Elemental analyis (%) calcd for $C_{24}H_{40}N_5Nb_2$: C 49.32, H 6.90, N 11.98; found C 48.94, H 6.71, N 11.83; IR (Nujol mull): $\tilde{\nu} = 1637$ (m), 1374 (s), 1341 (w), 1278 (w), 1260 (m), 1240 (s), 1195 (m), 1161 (w), 1103 (br. s), 1055 (s), 1053 (s), 1018 (s), 1015 (s), 949 (m), 871 (m), 836 (w), 822 (m), 801 (br. m), 790 (s), 730 (s), 670 (w), 641 (w) cm^{-1}; magnetic moment: $\mu_{eff} = 1.77\ \mu_B$; ^1H NMR (500 MHz, C_6D_6, 23 °C): $\delta = 9.2$ (br. s, 2H, bridging CH_2), 5.59 (s, 4H, CH-pyrrole), 4.91 (br. s, 1H, hydride), 1.85 (s, 12H, Me-pyrrole). .

Crystal structure analyses: **1**: $C_{62}H_{105}Cl_5N_{11}Nb_4Li$, $M_r = 1560.40$, triclinic $P\bar{1}$, $a = 12.295(3)$, $b = 14.916(3)$, $c = 20.818(5)$ Å, $\alpha = 96.763(4)$, $\beta = 91.542(4)$, $\gamma = 107.375(4)°$, $V = 3610(1)$ Å^3, $Z = 2$, $\rho_{calcd} = 1.435$ Mg m^{-3}, absorption coefficient 8.48 cm^{-1}, $F(000) = 1612$, reflections collected 10255, independent reflections 10228, GOF = 1.058, $R = 0.0385$, $wR^2 = 0.1061$. All non-hydrogen atoms were located and refined anisotropically. Hydrogen atoms were introduced at their idealized positions and refined with a riding mode. Two molecules of toluene per unit formula were located in the lattice. **2:** $C_{24}H_{40}N_5Nb_2$, $M_r = 584.43$, monoclinic *C2/c*, $a = 18.387(4)$, $b = 15.314(3)$, $c = 18.971(4)$ Å, $\beta = 110.377(3)°$, $V = 5007(2)$ Å^3, $Z = 4$, $\rho_{calcd} = 1.550$ Mg m^{-3} Absorption coefficient 9.36 cm^{-1}, $F(000) = 2408$, reflections collected 3571, independent reflections 3270, GOF = 1.192, $R = 0.0332$, $wR^2 = 0.0874$. All non-hydrogen atoms were located and refined anisotropically. The hydrogen atoms attached to C(1) as well as the hydride were located from the difference map. All the hydrogen atoms were refined with a riding model. Crystallographic data (excluding structure factors) for the structures reported in this paper have been deposited with the Cambridge Crystallographic Data Center as supplementary publication no. CCDC-101719 (**1**) and CCDC-101720 (**2**). Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (fax: (+44) 1223-336-033; e-mail: deposit@ccdc.cam.ac.uk).

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Valence Tautomerism in a *o*-Benzoquinone Adduct of a Tetraazamacrocycle Complex of Manganese**

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Among the molecular systems that exhibit electronic bistability, the *o*-benzoquinone–metal complexes, which are characterized by valence tautomerism, are a relatively new class of compounds.[1–3] Their main attractiveness resides in the formal equivalence of their physical behavior with that of the well-known spin-crossover metal complexes, whose reversible transformations can be utilized for creating addressable memories.[4, 5] To date valence tautomerism has been found only for a family of molecular *o*-benzoquinone complexes of general formula $[M(N{-}N)(diox)_2]$ (M = Co, Mn; N–N = diazine ligand; diox = catecholato, semiquinone anion); the transition temperatures T_c range from 100 to 350 K. We have now found a class of compounds of general formula [ML(diox)]Y (M = Mn, Co; L = tetraazamacrocyclic ancillary ligand) in which the valence tautomers are charged and thus allow the transition temperature to be tuned by using suitable counterions Y; the Mn system is reported here.

The reaction between $[Mn(cth)Cl_2]$ (cth = (±)*l*-5,7,7,12,14,14-hexamethyl-1,4,8,11-tetraazacyclotetradecane) and the 3,5-di-*tert*-butylcatecholate dianion (dtbcat) under inert atmosphere yields the complex [Mn(cth)(dtbcat)]. Upon exposure to air the $[Mn(cth)(diox)]^+$ cation is formed as the initial oxidation product. If this cation is precipitated as the tetraphenylborate salt, a yellow-brown product (**1**) is obtained, whereas green microcrystalline **2** precipitates with perchlorate. Analysis gave the general formulas [Mn(cth)(diox)]Y (Y = BPh_4, ClO_4). The two compounds have different physical properties in the solid state, but the spectroscopic properties of their solutions are identical.

Single crystals suitable for X-ray diffraction analysis were obtained only for **1**. The structure of the cation is shown in Figure 1.[6] The Mn center is six-coordinate, the macrocyclic ligand is bound in a folded configuration, and the benzoquinone acts as bidentate ligand. The features of the coordination

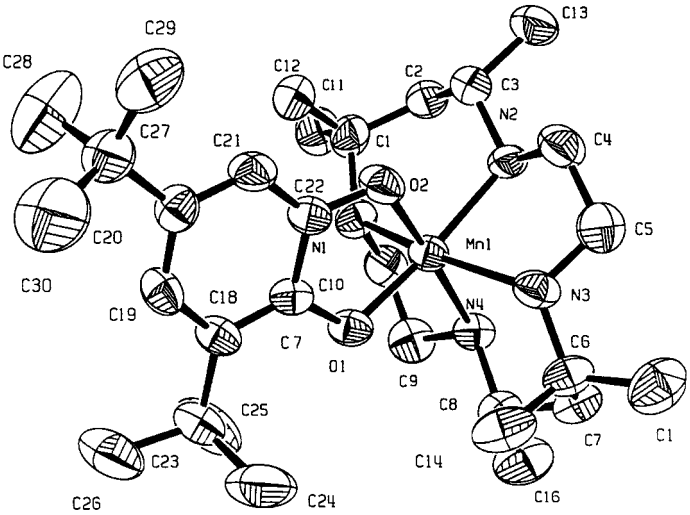

Figure 1. ORTEP plot of $[Mn(cth)(dtbcat)]^+$; the hydrogen atoms are omitted for clarity. Selected bond lengths [Å] and angles [°]: Mn–O1 1.881(4), Mn–O2 1.876(4), Mn–N1 2.311(5), Mn–N2 2.117(5), Mn–N3 2.313(5), Mn–N4 2.129(5), O1–C17 1.369(7), O2–C22 1.356(7), C17–C22 1.398(8); O1-Mn-O2 85.3(2), O1-Mn-N1 90.8(2), O1-Mn-N2 173.4(2), O1-Mn-N3 101.0(2), O1-Mn-N4 90.6(2), O2-Mn-N1 99.8(2), O2-Mn-N2 88.3(2), O2-Mn-N3 91.8(2), O2-Mn-N4 175.7(7).

polyhedron are fully consistent with the formulation of the cation as $[Mn^{III}(cth)(dtbcat)]^+$. The coordination geometry is strongly axially distorted, as expected for a high-spin d^4 electronic configuration. The M–N bond lengths are significantly longer for the apical nitrogen atoms than for the basal nitrogen atoms (2.31 and 2.12 Å, respectively) . The average Mn–O distance of 1.87 Å agrees well with those in other metal(III) catecholato derivatives.[7, 8] Finally, the structural parameters of the coordinated benzoquinone are typical of a catecholato dianion; the C–O and C–C bond lengths are similar to those observed for other dtbcat derivatives.[1]

The IR spectrum of **1** is virtually superimposable on those of the chromium, iron, and cobalt analogues, which can be

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