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Valence Tautomerism in a *o*-Benzoquinone Adduct of a Tetraazamacrocyclic 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 $[Mn(cth)Cl_2]$ ($cth = (\pm)l-5,7,7,12,14,14$ -hexamethyl-1,4,8,11-tetraazacyclotetradecane) and the 3,5-di-*tert*-butylcatechol 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

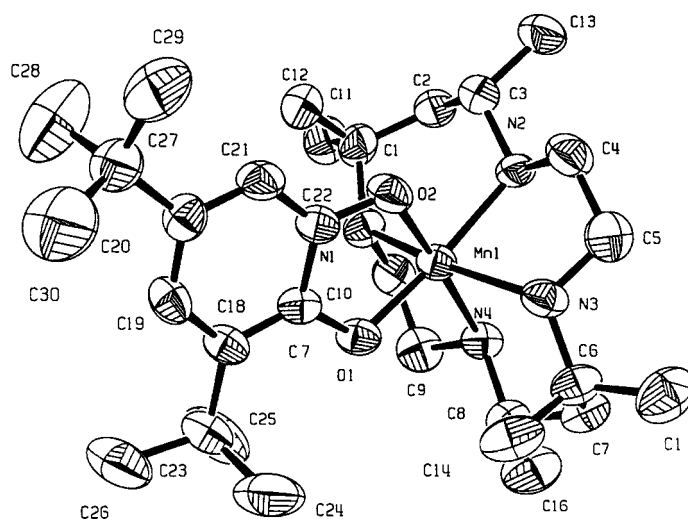


Figure 1. ORTEP plot of $[Mn(cth)(dtbcat)]^+$; the hydrogen atoms are omitted for clarity. Selected bond lengths [Å] and angles [°]: Mn–O1 1.881(4), Mn–O2 1.876(4), Mn–N1 2.311(5), Mn–N2 2.117(5), Mn–N3 2.313(5), Mn–N4 2.129(5), O1–C17 1.369(7), O2–C22 1.356(7), C17–C22 1.398(8); O1–Mn–O2 85.3(2), O1–Mn–N1 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 $Mn-N$ 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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unambiguously described as containing catecholato adducts of the trivalent metal ions.^[9] However, the physical properties of the green perchlorate salt **2** are consistent with semiquinonato (sq) character. Its IR spectrum is virtually superimposable on that of the nickel(II) and zinc(II) analogues, which can be unambiguously formulated as containing $[\text{M}^{\text{II}}(\text{cth})(\text{dtbsq})]^+$ cations ($\text{dtbsq} = 3,5\text{-di-}t\text{-butyl-}o\text{-semiquinone anion}$),^[10] and its reflectance spectrum indicates the presence of a semiquinonato chromophore.

The spectroscopic properties of both **1** and **2** are temperature-dependent. Heating solid **1** causes a reversible color change from yellow-brown to green, and cooling **2** in liquid nitrogen changes its color reversibly from green to yellow. Crystals of **1** are completely converted into the green form by heating for 1 h at 360–365 K under vacuum, and revert to the yellow-brown form after a few minutes at room temperature. The transition is noncooperative, as shown by the differential scanning calorimetry curve.

The electronic spectra of both compounds are strongly solvent-dependent (Figure 2). In highly polar solvents such as

DMSO, the spectra of the yellow solutions are consistent with the presence of an $[\text{Mn}^{\text{III}}(\text{cth})(\text{dtbcate})]^+$ chromophore, whereas in weakly polar solvents such as toluene or acetone the spectra of the blue-green solutions are consistent with the presence of a $[\text{Mn}^{\text{II}}(\text{cth})(\text{dtbsq})]^+$ chromophore. In the latter solvents, both the energies and the intensities of the bands at 13 000 and 25 700 cm^{-1} are similar to those of $[\text{Zn}^{\text{II}}(\text{cth})(\text{dtbsq})]^+$.^[10] The other bands can be reasonably attributed to metal-to-ligand charge transfer (19 000 and 23 300 cm^{-1}) and to d-d transitions involving some “trip multiplets” of the manganese(II) ion.^[11, 12] The electronic spectra therefore suggest that this manganese–benzoquinone adduct may be described by the two charge distributions $\text{Mn}^{\text{III}}\text{--cat}$ and $\text{Mn}^{\text{II}}\text{--sq}$, depending on the donor power of the solvent and the different solvation enthalpies of the two tautomers.^[13, 14]

Complex **1** has a χT value of 3.1 emu K mol^{-1} at 70–300 K, as expected for a d^4 metal ion in high-spin ground state (Figure 3). Below 70 K χT decreases and attains a value of 2.4 emu K mol^{-1} at 4.2 K. For **2**, χT decreases monotonically

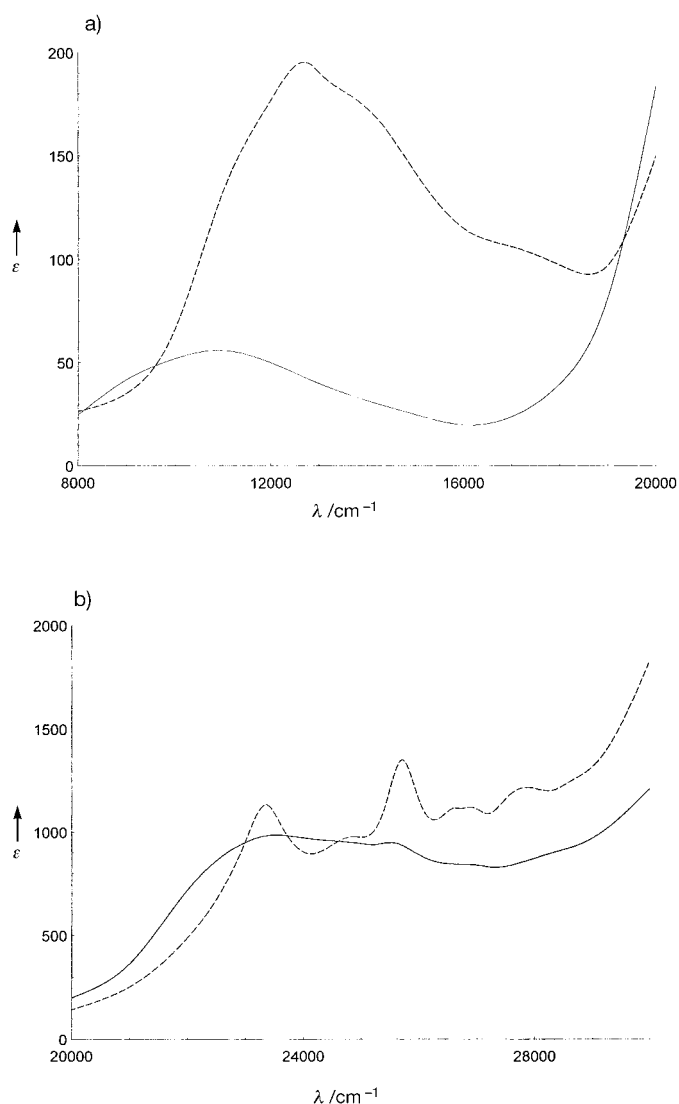


Figure 2. Electronic spectra of $[\text{Mn}(\text{cth})(\text{dtbcate})]\text{BPh}_4$ in acetone (---) and DMSO (—) in the range of 8000–20 000 cm^{-1} (a) and 20 000–30 000 cm^{-1} (b).

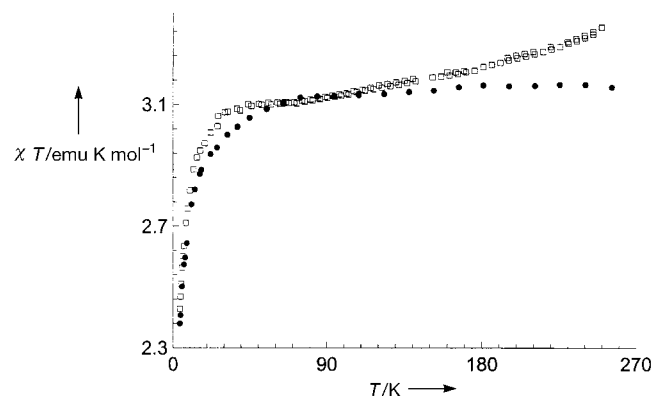


Figure 3. Change in χT as a function of temperature T for **1** (●) and **2** (□) in a magnetic field of 5000 G.

from 3.5 emu K mol^{-1} at 300 K to 3.1 emu K mol^{-1} at 90 K. Below 90 K the temperature dependence of **2** is similar to that of **1**, and a value of 2.4 emu K mol^{-1} is attained at 4.2 K. Since χT of **2** continues to increase at room temperature, at the high-temperature limit it greatly exceeds the value for a Mn^{III} ion. Therefore it can be suggested that at high temperature **2** is stable as $\text{Mn}^{\text{II}}\text{--sq}$. If the two paramagnetic species are not coupled, χT should be 4.75 emu K mol^{-1} . The decrease between 280 and 120 K might be due both to interconversion between the $\text{Mn}^{\text{II}}\text{--sq}$ and $\text{Mn}^{\text{III}}\text{--cat}$ forms and to antiferromagnetic coupling between the paramagnetic metal ion and the radical ligand.^[7, 8, 15] If the former were dominant, the interconversion process should be of the noncooperative type. The X-band EPR spectra of **1** and **2** at low temperatures show several features which may be due to impurities. High-field EPR investigations are in progress.

The system reported here follows the general pattern of valence tautomerism,^[1–3] in which an entropy-driven electron transfer process involves two species with nearly degenerate electronic states. The novelty of this system lies in the possibility of tuning the thermodynamics of the electron transfer process by varying the counterion.

Experimental Section

[Mn(cth)Cl₂] was prepared from [(NEt₄)₂MnCl₄] (5 mmol) and cth (6 mmol) in acetonitrile (30 mL). The reaction between dtbcat (1 mmol) and [Mn(cth)Cl₂] (1 equiv) in basic methanol (30 mL) under inert atmosphere gave [Mn(cth)(dtbcat)]. Crystals of **1** were obtained by adding an aereated solution of NaBPh₄ in methanol, and **2** by adding an aqueous solution of NaClO₄. The inert atmosphere was removed and the resulting suspensions were stirred for 1 h at room temperature. Complexes **1** and **2** were obtained in 80 and 70% yield, respectively.

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A Novel Beryllium Thiolate Resulting from N–Si Bond Cleavage: Liberation of Ammonia in the Reaction of Be[N(SiMe₃)₂]₂ with HSPH**

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In the course of our investigations into the synthesis and solid-state structures of alkaline earth metal thiolates, we have used the bis(trimethylsilyl)amides of beryllium, magnesium, and calcium as hydrocarbon-soluble metalating agents.^[1] We anticipated clean metathesis reactions between the metal amide and arenethiols with formation of the amine HN(SiMe₃)₂. Here we present results that indicate competitive acid/base reactions between hexamethyldisilazane and unchanged thiol in the reaction of [Be{N(SiMe₃)₂}]₂ with stoichiometric amounts of HSPH in the presence of Lewis bases.

The chemistry of the beryllium–oxygen bond is by far the most extensively studied interaction between beryllium and another element.^[2] In contrast, information on beryllium thiolates is scarce. In the only crystallographically characterized homoleptic beryllium thiolate, the sterically demanding SMes* ligand (SMes* = S-2,4,6-*t*Bu₃C₆H₂) afforded the three-coordinate monomer [Be(thf)(SMes*)₂].^[3] A three-coordinate monomeric structure was also identified in the mixed alkylberyllium thiolate [Be(2,6-Mes₂C₆H₃)(SMes*)(Et₂O)] (Mes = 2,4,6-Me₃C₆H₂), in which the metal center is also stabilized by bulky ligands.^[4] A four-coordinate beryllium center was found in [Be(S₂CNIPr₂)₂], in which both dithiocarbamate ligands chelate the cation through the two thiolato groups.^[5] Finally, a small family of alkylberyllium thiolate compounds have been shown by ¹H NMR spectroscopy and cryoscopic measurements to exist as monomeric or oligomeric complexes, depending on the combination of ligands and donor, although detailed structural data are not available.^[6] Here we report the synthesis and characterization of the novel, ammonia-coordinated, crown ether templated beryllium thiolate [[Be(SPh)₂(py)(NH₃)₂][[18]crown-6]] · 2 C₇H₈ (**1**; py = pyridine), which is formed by a sequence of acid-promoted N–Si bond cleavage reactions and in situ trapping of the liberated ammonia.

The reaction of [Be{N(SiMe₃)₂}]₂^[7] with two equivalents of HSPH in toluene in the presence of [18]crown-6 gave a thick, white suspension; addition of one equivalent of pyridine generated a homogenous solution,^[8] from which **1** was obtained as colorless crystals, which were analyzed by single-crystal X-ray diffraction. The identity of **1** was also

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