

## Synthesis and X-Ray Crystal Structure of Dipotassium [Tris(3,5-di-*t*-butylpyrocatecholato)manganate(IV)]–Acetonitrile (1/6), a Novel Mn<sup>IV</sup> Tris(bidentate) Chelate

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The structure of the dipotassium salt of the tris(3,5-di-*t*-butylpyrocatecholato)manganate dianion consists of a trigonally distorted tris(bidentate) chelate with two sets of Mn–O distances [1.922(3) and 1.891(3) Å], and appears more consistent with an Mn<sup>IV</sup>–pyrocatecholate formulation than an Mn<sup>III</sup>–semiquinone.

Despite its implication in the water oxidation site of photosystem II, the co-ordination chemistry of tetravalent manganese is largely a matter of conjecture. The paucity of reports on Mn<sup>IV</sup> complexes<sup>1,2</sup> testifies to the powerfully oxidizing character of this species. Since pyrocatechol (*o*-dihydroxybenzene) has a pronounced ability to stabilize metal ions in high oxidation states (*e.g.*, Ce<sup>IV</sup>, ref. 3), we considered it likely that complexation of Mn<sup>IV</sup> with pyrocatechol might afford an opportunity to isolate a complex of the little-studied tetravalent state of manganese. Furthermore, isolation of a tractable, stable Mn<sup>IV</sup> complex might provide a useful entry point into the synthesis of other complexes of tetravalent manganese, and thereby facilitate exploration of Mn<sup>IV</sup> chemistry.

Recently Sawyer and co-workers<sup>4,5</sup> reported that mixtures of Mn(acac)<sub>3</sub> (acac = acetylacetonato), 3,5-di-*t*-butylpyrocatechol, and 3,5-di-*t*-butyl-*o*-benzoquinone in the presence of base gave a deep blue complex, which was formulated as [MnL<sub>3</sub>]<sup>2-</sup> where L = 3,5-di-*t*-butylpyrocatecholato (generated in solution and not isolated). This complex was initially thought to bind dioxygen reversibly,<sup>4,5</sup> but this suggestion has subsequently been shown to be in error.<sup>6</sup>

We have synthesized the tris(3,5-di-*t*-butylpyrocatecholato)manganate dianion isolated as its K<sup>+</sup> salt, and determined its structure by X-ray diffraction. *A priori*, this dianion may be formulated either as Mn<sup>IV</sup>–tris(pyrocatecholate) or Mn<sup>III</sup>–mono(semiquinone)–bis(pyrocatecholate). From the results reported herein, it appears that the tris(3,5-di-*t*-butylpyro-

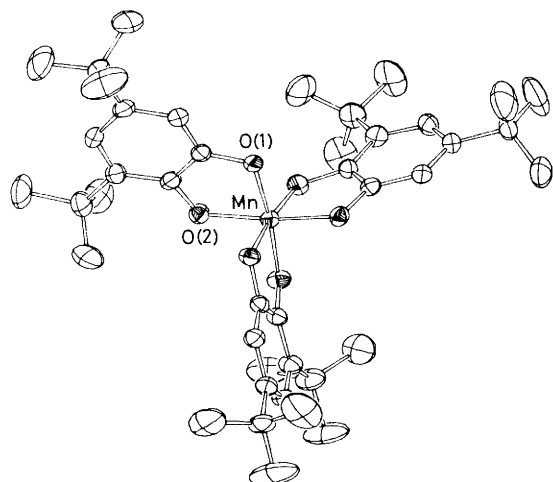
catecholato)manganate dianion represents a novel example of a Mn<sup>IV</sup> chelate.

The title compound was synthesized by treatment of Mn(acac)<sub>3</sub> with an alkaline (KOH) solution of 3,5-di-*t*-butylpyrocatechol in MeOH to give a red–brown solution, which was evaporated, and the residue taken up in MeCN. After filtration (to remove undissolved K<sup>+</sup> acac<sup>-</sup>), addition of 1 equiv. of I<sub>2</sub> caused the red–brown solution to become deep blue, whereupon the deep blue product crystallized immediately. Re-crystallization from hot MeCN afforded crystals of the hexasolvate as dark blue rhombohedral prisms, suitable for X-ray analysis.†

*Crystal data:* C<sub>42</sub>H<sub>60</sub>K<sub>2</sub>MnO<sub>6</sub>·6CH<sub>3</sub>CN, *M* = 1040.40, hexagonal, space group  $R\bar{3}$ , *a* = 14.760(9), *c* = 50.752(32) Å; 1838 unique reflections with  $F_0^2 > 3\sigma(F_0^2)$  were measured with Mo-*K*<sub>α</sub> radiation on a Syntex R3m diffractometer. The structure was solved by heavy atom methods and refined by block-diagonal least-squares with anisotropic thermal parameters for all non-hydrogen atoms to *R* = 6.9% (*R*<sub>w</sub> = 7.1%).‡

† Physical properties: λ<sub>max</sub> 590 nm (ε *ca.* 5000); μ(313 K) = 3.8 B.M.

‡ The atomic co-ordinates for this work are available on request from the Director of the Cambridge Crystallographic Data Centre, University Chemical Laboratory, Lensfield Road, Cambridge CB2 1EW. Any request should be accompanied by the full literature citation for this communication.



**Figure 1.** Molecular structure of the tris(3,5-di-*t*-butylpyrocatecholato)manganate(IV) dianion.

The structure of dipotassium [tris(3,5-di-*t*-butylpyrocatecholato)manganate]acetonitrile (1/6) consists of *cis*-[tris(3,5-di-*t*-butylpyrocatecholato)manganate]<sup>2-</sup> units (Figure 1) with a twist angle of 52°; hence the dianion in this salt has a geometry much closer to octahedral (60°) than trigonal prismatic (0°). The Mn–O distances are 1.922(3) and 1.891(3) Å, with an O–Mn–O bite angle of 85.2(1)°. The average C–O distance is 1.362(5) Å, in the range found for other metal-catecholate C–O bonds; other bond distances and angles of the pyrocatechol rings are normal. The two K<sup>+</sup> ions are found on either side of a dianion to form a linear K<sup>+</sup>–Mn–K<sup>+</sup> array along the crystallographic 3-fold axis, and are co-ordinated to three pyrocatechol oxygen atoms on one side [K<sup>+</sup>–O (av) 2.77 Å] and three symmetry-equivalent MeCN nitrogen atoms on the other [K<sup>+</sup>–N (av) 2.85 Å].

The crystallographic data (including the apparent lack of disorder) support the Mn<sup>IV</sup>-tris(catecholate) structure over the alternative Mn<sup>III</sup>-mono(semiquinone)-bis(pyrocatecholate) formulation. Thus the C–O bond lengths are typical of metal-pyrocatecholates<sup>7</sup> [*e.g.*, 1.349(3) Å for the tris(pyrocatecho-

lato)chromium trianion<sup>8</sup>; *cf.* 1.285(8) Å for tris(3,5-di-*t*-butyl-*o*-benzosemiquinone)chromium<sup>9</sup>], the phenyl rings lack the distortion typical of semiquinones,<sup>7</sup> and the Mn–O distances are short for an Mn<sup>III</sup>-semiquinone complex. Furthermore, there is no evidence for either static or dynamic Jahn–Teller distortion (as would be anticipated for high spin Mn<sup>III</sup>, d<sup>4</sup>). No tetragonal distortion of the Mn co-ordination sphere is observed, and the thermal parameters of the pyrocatechol oxygen atoms are neither particularly large nor anisotropic. [The observed trigonal distortion of the Mn co-ordination sphere does not reflect Jahn–Teller splitting, because a trigonal distortion does not lift the degeneracy of the e<sub>g</sub> (in O<sub>h</sub>) orbitals.] For these reasons, the Mn<sup>IV</sup>-tris(pyrocatecholate) formulation seems appropriate.

The present results indicate that complexation by pyrocatechol effectively stabilizes even Mn<sup>IV</sup> to afford a rare example of an Mn<sup>IV</sup> co-ordination complex.

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