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An Example of Nitroso Oxygen-to-Metal Bonding: X-Ray Molecular Structure of Dichlorodimethylbis(4-nitroso-N,N-dimethylaniline)tin(IV)

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Coordination mode in metal complexes with C-nitroso ligands is of interest since the nitroso group is isoelectronic with dioxygen, diazenes, and carbonyl compounds. However, there is only limited structural work for these complexes. Of some proposed binding modes of RN=O ligand to metal ions, two modes have been structurally characterized; monodentate N-bonding [1–3], and coordination by both nitrogen and oxygen atoms [4, 5]. On the other hand, monodentate O-bonding has been proposed for several metal complexes with 4-nitroso-N,N-dimethylaniline (NODMA) on the basis of spectroscopic data [6, 7]. However, $Co^{II}Cl_2(NODMA)_2$ which had been spectroscopically estimated to be oxygen-bonding [6], was recently concluded by X-ray structure analysis [3] to be a nitrogen bonded complex. Thus, to date there is no convincing evidence for the existence of metal complexes with monodentate oxygen-bonded C-nitroso ligands. Previously one of the authors has suggested on the basis of electronic absorption spectra that NODMA coordinates to dichlorodimethyltin(IV) through oxygen in solution [8]. In order to realize the existence of nitroso oxygen-to-metal bonding, we have investigated the crystal structure of dichlorodimethylbis(NODMA)tin(IV).

To a benzene solution of dichlorodimethyltin(IV) was added 2.5 molar amounts of NODMA in benzene. The precipitates obtained immediately were recrystallized from benzene to give red columns of $Cl_2Me_2(NODMA)_2Sn^{IV}$, m.p. 139–140 °C, *Anal.* Found: C, 41.71; H, 5.20; N, 10.73%. Calcd. for $C_{18}H_{26}N_4O_2Cl_2Sn$: C, 41.57; H, 5.04; N, 10.77%.

Crystal data for $Cl_2Me_2(NODMA)_2Sn^{IV}$: Triclinic, space group $P\bar{1}$ $a = 7.182(1)$, $b = 8.728(1)$, $c = 9.307(1)$ Å; $\alpha = 90.91(1)$, $\beta = 109.65(1)$, $\gamma = 90.94(1)^\circ$; $U = 549.2(1)$ Å^3, $Z = 1$, $D_x = 1.572$ g cm^{-3}, $F(000) = 262$, $\mu(\text{Mo-K}\alpha) = 10.5$ cm^{-1}. A specimen, approximately 0.15 × 0.18 × 0.24 mm, was used for analysis. The intensity data were collected on an automated diffractometer with graphite-monochromatized Mo-Kα radiation. The structure was solved by the standard heavy-atom method and refined by the block-diagonal least-squares procedure. Anisotropic thermal vibrations were assumed for all the nonhydrogen atoms. Hydrogen atoms, except for those of N-methyl groups, were revealed from a difference Fourier map and refined isotropically. The N-methyl hydrogen atoms were not found, due to large thermal vibrations of the N-methyl carbons. The R value was 0.052 for 4023 independent reflections with $|F_o| > 3\sigma(F)$.

The crystal structure consists of a discrete, centrosymmetric molecule per unit cell. Figure 1 illustrates the molecular structure of the complex. Two chlorine atoms, two methyl groups and two nitroso ligands form an octahedral coordination around the tin atom. The NODMA ligands coordinate to tin through their nitroso oxygen atoms. The present complex is the first example having monodentate oxygen-bonding by C-nitroso ligands well characterized by X-ray analysis. This coordination mode is in contrast to the metal-to-nitrogen bonding in $Pd^{II}Cl_2$-

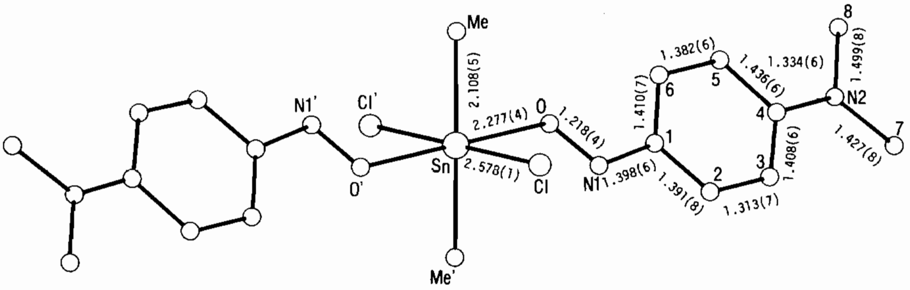

Fig. 1. Molecular structure of $Cl_2Me_2(NODMA)_2Sn^{IV}$. The Sn atom lies on a center of symmetry. Bond distances (in Å) are shown with e.s.d. s in parentheses. Relevant bond angles (in °) are: Cl–Sn–C(Me), 89.7(1); O–Sn–C(Me), 94.3(2); Cl–Sn–O, 92.27(9); Sn–O–N(1), 120.3(3); O–N(1)–C(1), 112.9(4); N(1)–C(1)–C(2), 113.0(4); N(1)–C(1)–C(6), 127.2(5); C(7)–N(2)–C(8), 115.8(5).

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$(C_6H_5NO)_2$ [1] and $Co^{II}Cl_2(NODMA)_2$ [3]. Sn–C and Sn–Cl bond distances are in the regions (2.07–2.23 and 2.43–2.64 Å respectively) of those observed in other dichlorodimethyltin(IV) [9]. The Sn–O distance is close to that (2.251(16) Å) of dichlorodimethylbis(pyridine N-oxide)tin(IV) [10], where two chlorine atoms occupy the *trans* positions to one another as well as two oxygen atoms and two methyl groups, the geometry around the tin atom being very similar to that of the present complex. Although O, N(1), N(2) and the phenyl ring are almost coplanar, Sn deviates by 0.15 Å from the plane.

Previously the decrease of the infrared ν(N=O) frequency of NODMA in the metal complexes was considered to be evidence that NODMA coordinates to the metal ions through nitroso oxygen [6, 7]. However, the X-ray analysis of $Co^{II}Cl_2(NODMA)_2$ indicated the presence of the nitroso nitrogen-to-metal bonding, although the ν(N=O) frequency (1499 cm^{-1}, KBr disk) of this complex occurred at 27 cm^{-1} lower frequency than that of NODMA. On the other hand, the present complex having the nitroso oxygen-to-metal bonding has exhibited the ν(N=O) band at 1563 cm^{-1} (in a Nujol mull), which is 36 cm^{-1} higher than the frequency of free NODMA. This finding appears to correspond to the rather shorter N–O bond distance (1.218(4) Å) of the complex in comparison with that of $Co^{II}Cl_2(NODMA)_2$ (1.267(5) Å).

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