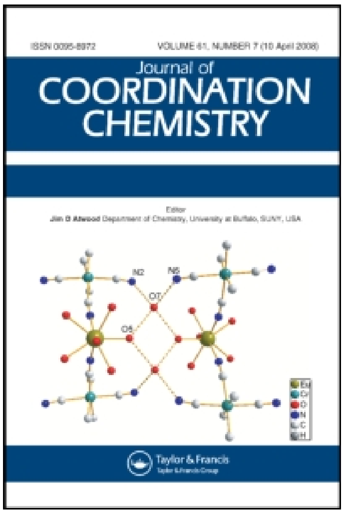

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Apparent Five-Coordinate Metal Complexes: Evidence for Trifunctional Bridge Bonding with the 3-Cyano-2,4-Pentanedionate Ligand in the Trichloro(3-Cyano-2,4-Pentanedionato) Complexes of Tin(IV) and Titanium(IV)

D. W. Thompson[a]; P. B. Barrett[a]; J. P. Lefelhocz[a]; G. A. Lock[a]
[a] Department of Chemistry, College of William and Mary, Williamsburg, Virginia

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SHORT COMMUNICATION

Apparent Five-Coordinate Metal Complexes: Evidence for Trifunctional Bridge Bonding with the 3-Cyano-2,4-Pentanedionate Ligand in the Trichloro(3-Cyano-2,4-Pentanedionato) Complexes of Tin(IV) and Titanium(IV)

D. W. THOMPSON, P. B. BARRETT, J. P. LEFELHOCZ and G. A. LOCK

Department of Chemistry, College of William and Mary, Williamsburg, Virginia 23185

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Sir:

We wish to report evidence for an oligomeric structure in trichloro(3-cyano-2,4-pentanedionato) titanium(IV), Cl_3TiL, and trichloro(3-cyano-2,4-pentanedionato)tin(IV), Cl_3SnL. Evidence is presented that oligomerization is accomplished by a novel bridging interaction involving the planar trifunctional 3-cyano-2,4-pentanedionate anion.

Titanium tetrachloride and tin tetrachloride react with 3-cyano-2,4-pentanedione[1] in a 1 : 1 molar ratio in methylene chloride to yield Cl_3TiL and Cl_3SnL, respectively. *Anal.* Calcd for $C_6H_6Cl_3NO_2Ti$:C, 25.89; H, 2.17; Cl, 38.20. Found: C, 25.75; H, 2.31; Cl, 38.16. Mp: Does not melt below 300°. Molar conductivity: $4.4 cm^2 ohm^{-1} mol^{-1}$ in acetonitrile[2]. *Anal.* Calcd for $C_6H_6Cl_3NO_2Sn$: C, 20.64; H, 1.73; Cl, 30.46; Sn, 33.99. Found: C, 20.83; H, 1.63; Cl, 30.33; Sn, 34.23. Mp: Does not melt below 300°. (Unfortunately both complexes are insoluble in nondestructive solvents, and therefore characterization was limited primarily to the solid state.)

The reaction of $TiCl_4$ with 3-cyano-2,4-pentanedione in a 1 : ~2.5 molar ratio, respectively, yields the disubstituted product dichlorobis(3-cyano-2,4-pentanedionato)titanium(IV). *Anal.* Calcd for $C_{12}H_{12}Cl_2N_2O_4Ti$: C, 39.28; H, 3.25; Cl, 19.35. Found: C, 39.46, H, 3.25; Cl, 18.64. Mp: Decomposes ca. 195°. Molar conductivity: $0.3 cm^2 ohm^{-1} mol^{-1}$ in nitrobenzene. Ir and temperature dependent nmr spectra show that this complex has the expected *cis* configuration. It is pertinent to note the reaction of $TiCl_4$ with3-cyano-2,4-pentanedione in a one to less than ca. 2.5 molar ratio yields a mixture of Cl_3TiL and Cl_2TiL_2. This is to be contrasted with the facile formation of several dichlorobis(β-diketonato)titanium(IV) complexes from $TiCl_4$ and β-diketones in approximately 1 : 2 molar ratios.[3,4] Furthermore, both Cl_3TiL and Cl_2TiL_2 are bright yellow solids whereas all other trichloro(β-diketonato)titanium(IV) complexes are much darker (very deep reds) than their dihalobis(β-diketonato)titanium(IV) counterparts (orange to red)[4,5] These observations although qualitative, do raise the possibility that Cl_3TiL may have a different molecular structure compared with other known trichloro(β-diketonato)titanium(IV) complexes.

In contrast to the $TiCl_4$—3-cyano-2,4-pentanedione system, $SnCl_4$ when allowed to react with 3-cyano-2,4-pentanedione in refluxing benzene in a 1 : ~2.5 molar ratio, respectively, yields only the monosubstituted product Cl_3SnL!

The isolation of Cl_3SnL and the inability to prepare Cl_2SnL_2 was quite surprising. All previous work with $SnCl_4$ and β-diketones led only to the isolation of bis(β-diketonato)dihalotin(IV) complexes.[6,7] In fact, deliberate attempts to force the formation of trihalo(β-diketonato)tin(IV) complexes have failed; for example, attempts to react $SnCl^4$ and 2,4-pentanedione in molar ratios up to 5 : 1, respectively, resulted only in formation of the bis-(2,4-pentanedionato)-product.[6,8] Thus, the synthetic results in the tin tetrachloride—3-cyano-2,4-

pentanedione system intimate that the 3-cyano-2,4-pentanedionate anion functions differently (i.e., to stabilize a Cl_3SnL species) than do the typical difunctional oxygen-chelating β-diketonate ligands. Spectral data support this intimation (vide infra).

The ir spectra[9] of the titanium and tin trihalo complexes show strong broad bands in the 1500–1600 cm^{-1} region with no bands from 1600–1800 cm^{-1}. This unambiguously establishes that the 3-cyano-2,4-pentanedionate anion is chelated to a metal center through the oxygen atoms. Also, for each complex a single sharp band in the cyanide stretching is observed. Interestingly however, is the fact that for the titanium complex the cyanide stretching frequency is observed at 2242 cm^{-1} and for the tin complex at 2234 cm^{-1}, whereas 3-cyano-2,4-pentanedione exhibits $\nu_{C\equiv N}$ at 2219 cm^{-1} which is in agreement with Fackler[10] who found $\nu_{C\equiv N}$ to be at 2220.4 cm^{-1} in $CHCl_3$ and 2218.9 cm^{-1} in KBr. We interpret the increase in $\nu_{C\equiv N}$ in the tin and titanium complexes relative to free 3-cyano-2,4-pentanedione ($\Delta\nu_{C\equiv N} = 15$ and 23 cm^{-1}, respectively) as being due to interaction of the cyanide group of an oxygen chelated 3-cyano-2,4-pentanedionate ligand with the metal center of a second Cl_3ML monomeric unit. It has been established that coordination of nitriles to metal centers through nitrogen gives rise to an increase in $\nu_{C\equiv N}$.[11] For example, coordination of phenyl cyanide to $TiCl_4$ and $SnCl_4$ results in positive frequency shifts relative to the free nitrile of 45 cm^{-1} and 29 cm^{-1}, respectively.[12]

One could object to the interpretation that the cyanide group of an oxygen-chelated 3-cyano-2,4-pentanedionate ligand is coordinated to a second metal center on the basis that the changes observed in $\nu_{C\equiv N}$ are simply a result of a perturbation arising from replacement of the enolic hydrogen of the free ligand by a metal. This explanation can be rejected for several reasons. First, as mentioned we have synthesized the monomeric six-coordinate dichlorobis(3-cyano-2,4-pentanedionato)titanium(IV) for which the cyanide stretching mode is centered at 2223 cm^{-1}. (Very small splitting, 5 cm^{-1}, is observed which is consistent with C_2 symmetry of the *cis* configuration.) Second, we synthesized triethylammonium trichloro-*n*-butyl-(3-cyano-2,4-pentanedionato)stannate(IV) in which no cyanide coordination is expected and in which $\nu_{C\equiv N}$ is displayed at 2220 cm^{-1}. Third, six oxygen-chelated tris(3-cyano-2,4-pentanedionato)metal(III) complexes, metal = Fe, Cr, Co, Al, Ga, and In, show cyanide stretching frequencies at 2216.0, 2216.3, 2216.6, 2217.2, 2217.5, and 2215.4 cm^{-1}.[10] Thus, it appears that in hexa-coordinate metal complexes the metal center does not effect the cyanide stretching mode.

Further evidence for the claim of cyanide coordination at the available sixth ligand site of a monomeric Cl_3TiL unit comes from the low frequency ir spectrum. X-ray analysis has shown that trichloro (2,4-pentanedionato)titanium(IV) is dimeric in the solid state being bridged by chloride ligands.[13] The low frequency ir spectra for this complex shows two prominent bands at 276 and 246 cm^{-1} which have been assigned to bridging Ti-Cl stretching modes by comparison with spectra for non-bridging $Cl_2Ti(C_5H_7O_2)_2$ and the bridging $[(C_2H_5)_4N][Ti_2Cl_9]$. In comparison the ir spectrum (510–200 cm^{-1}) for Cl_3TiL reveals bands only at 410 m, 455 s, 390 vs, br, and 310 w. The absence of bands from 300–200 cm^{-1}, the region for bridging Ti-Cl stretching modes, supports the claim that Cl_3TiL differs structually from trichloro(2,4-pentanedionato)titanium(IV) and that the six-coordination is obtained by means of planar trifunctional bridging behaviour of the 3-cyano-2,4-pentanedionate ligand.

The observation of a single cyanide band shifted to higher frequency for both Cl_3SnL and Cl_3TiL is consistent with the presence of coordinated cyanide

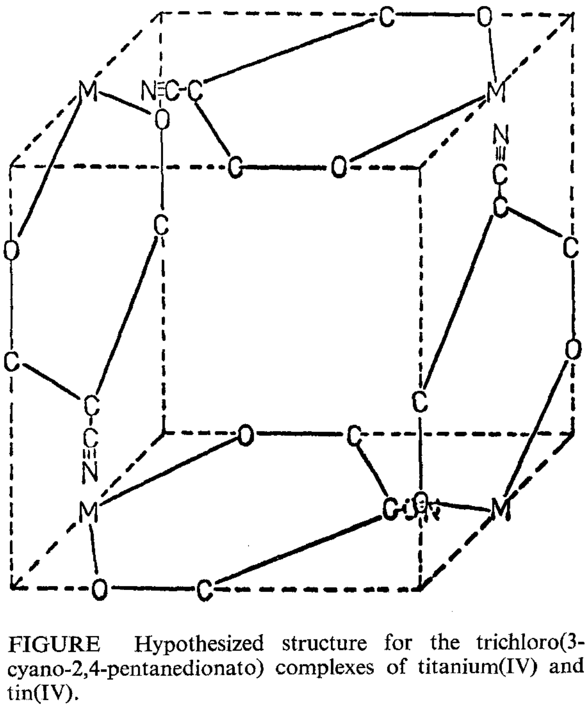

FIGURE Hypothesized structure for the trichloro(3-cyano-2,4-pentanedionato) complexes of titanium(IV) and tin(IV).

groups only. Thus a symmetrical cyclic oligomeric structure rather than an open structure is suggested. Molecular models indicate that a reasonable structure for the two complexes under consideration which preserves the tendency for titanium(IV) and tin(IV) complexes to exhibit octahedral-type coordination is that of a cyclic tetramer illustrated in the Figure. The cyclic tetrameric structure has precedent in the dialkygold cyanides[14] which have been shown to have this structure. Furthermore, the 1 : 1 adduct formed between dicyanobis(*o*-phenanthroline)iron(III) and germanium tetrafluoride has been assigned a tetrameric-like structure.[15]

The Mossbauer (Sn^{119m}) spectrum of Cl_3SnL displays a single symmetrical peak having a isomer shift of 0.40 mm sec^{-1} and a line width of 1.17 mm sec^{-1}. This result is consistent with but not conclusive for, a single tin environment such as would exist in a cyclic tetramer.

We are extending studies to several other metal-3-cyano-2,4-pentanedionate systems which are capable of forming apparently coordinatively unsaturated monomeric units. Furthermore, although thus far we have been unsuccessful in producing crystals of the title complexes suitable for X-ray analysis, we are continuing efforts in this regard.

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