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First Report on Thermally Stable Cadmium Carbonyl Complex Containing an Interesting Chloroaryl Bridge: Isolation and Characterization

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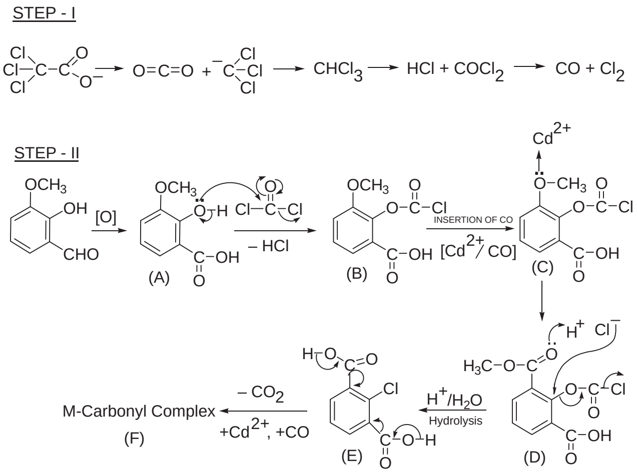
A novel thermally stable tetranuclear cadmium carbonyl complex $[Cd(CO)_3(C_6H_3Cl)]_4 \cdot 2H_2O$ has been synthesized for the first time through a green path with an overall yield of 35%. The synthetic route features a new pathway, creating the two ortho-positions with respect to the chlorine atom in the aryl rings for bridging two cadmium metal centers. The title complex has been characterized by microanalytical, infrared spectroscopic, and thermal methods while its structure has been established by single-crystal X-ray diffraction supported by ^{1}H, ^{13}C, and ^{113}Cd NMR data.

Increasingly demanding environmental legislation and the resulting drive toward clean technology in the chemical industry, "enviroeconomics" will become a driving force behind new products and processes. Today carbonylation processes are used extensively,[1–3] for example, the oxo and Monsanto processes. Over the past years, a series of carbonyl complexes of divalent metal ions have been reported, especially for 1st and 2nd series transition-metal ions. Zinc and cadmium metal ions are more electropositive than their neighbors in the transition series and show some resemblances to the d-block elements in their ability to form complexes, particularly with ammonia, amines, halide, and cyanide ions. However, for complexes even with cyanide ion, it must be borne in mind that the possibility of d_π bonding between these metal ions and the ligand is very much lowered compared to their transition analogs simply owing to their electronic structure. In fact, carbonyl, nitrosyl, olefin complexes, etc., of the type given by transition metals are not known so far for either zinc or cadmium ion. Moreover, the coordination of aromatic hydrocarbons to transition metal is of considerable interest in organometallic chemistry.[4] Aromatic systems can act as ligands for group III and lanthanoid elements, although the intrinsic electropositive nature of these metal ions indicates that the bonding is best described as ionic with the arene ligands formally carrying considerable negative charge.[5–7] Efforts to make polymetallic aromatic complexes are frequently frustrated due to the difficulty of introducing the aromatic component in the coordination sphere of the metal, especially for cadmium ion. Investigation of polymetallic aromatic compounds has been done by many authors.[8] We have tried several times to prepare polymetallic aromatic carbonyl complex by passing carbon monoxide directly to the reaction medium under different reaction conditions but failed. To achieve this goal, we have adopted a method of in situ formation of carbon monoxide in the reaction system and were successful in isolating the novel tetranuclear organocadmium complex reported herein. To the best of our knowledge, it is the first reported complex of the cadmium–carbonyl class.



Scheme 1. Plausible mechanistic path for the formation of the title complex.

We treated an aqueous-methanolic solution of cadmium(II) trichloroacetate with *o*-vanillin, which forms the reported novel organocadmium complex.[9]

The most plausible mechanism for the formation of this novel carbonyl complex with a fascinating structural moiety has been delineated in Scheme 1, consisting of two steps (Step I and Step II) as shown above.

In the first step trichloroacetate anion on heating at around 60 °C with water–methanol (1:10) mixture gives chloroform,[10] which in the presence of sunlight decomposed to give carbon monoxide. In the second step oxidation of *o*-vanillin gives vanillic acid (A) which undergoes subsequent chloroformylation (B), esterification (C), and chlorination (D) followed by simultaneous hydrolysis (E) and decarboxylation (F) leading to the titled cadmium carbonyl complex. The esterification of the methoxy group is facilitated due to the coordination of Cd^{2+} ion, which acts as a Lewis acid through coordination of the methoxy oxygen favoring the insertion of a carbonyl group. The striking observation is that here CO acts as an oxidizing species in converting methoxy (–OMe) to ester (–COOMe) and also simultaneously acts as an electron-pair donor ligand. In the presence of acid, the carbonyl oxygen of the ester group becomes protonated and then undergoes hydrolysis via bimolecular acid-catalyzed mechanism in which acyl oxygen bond cleavage occurs and the OMe group is eliminated as MeOH. The spontaneous degradation of E with the C–C bond cleavage via decarboxylation is facilitated by the electron-withdrawing effect of chlorine, which generates 2,6 binegative chloroaryl ion. This binegative chloroaryl ion acting as a nucleophilic ligand toward

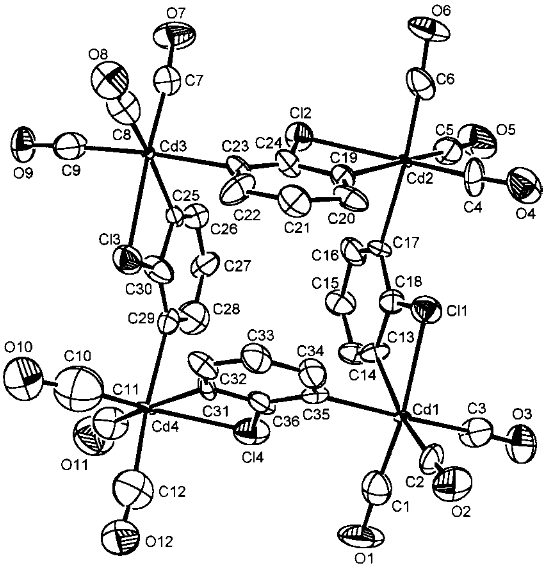


Figure 1. ORTEP plot of the title complex (**1**).

the cadmium metal ion present in the system resulted in the expected compound.

The presence of carbonyl in the complex was confirmed by IR spectroscopy. The absorption band attributed to the terminal carbonyl groups appeared in the region 2120–2245 cm^{-1} [2225(s), 2190(s), 2245(m), and 2120(w)], typical for tricarbonyl stretching.[11] Elemental analysis[9] and spectral studies confirm the 1:1 stoichiometry between Cd^{II} and bridging ligand. NMR spectroscopic data[12] confirm the symmetric structure of the complex. The positive chemical shift ($\delta + 37.11$ ppm) of ^{113}Cd strongly supports the attachment of donating ligands with the metal. A TGA study of the complex in a dynamic nitrogen environment shows the elimination of two molecules of lattice water in a single step within 45–60 °C. Later on the decomposition of the anhydrous complex started at 80 °C with the elimination of carbon monoxide followed by decomposition. The liberation of carbon monoxide has been confirmed by qualitative test.

X-ray crystallographic[13] studies revealed that the complex, a square-shaped tetramer, consists of $[Cd(CO)_3(C_6H_3Cl)]_4$ units linked by chloroaryl ligands, as shown in Figure 1. There are also two water molecules per complex in the crystal lattice. The occupancy of water molecules is partial and disordered. Within a given tetramer, each chloroaryl ligand acts as a chelate to one cadmium atom through the chlorine and one ortho carbon while the other ortho carbon with respect to chlorine substituent of the aryl group is utilized to form a bridge with another cadmium atom. The chloroaryl ligands act as the four edges of the square defined by the four cadmium atoms. The four chloroaryl ligands may be divided into two sets. Two ligands in each set are slightly tilted with respect to each other. The closest C–C separations between two chloroaryl rings of two sets are 3.356 (C15–C27) and 3.478 Å (C21–C33), while with respect to their coordinating ends the C–C separations are 5.381 (C18–C30) and 5.409 Å (C24–C36). However, the ring planes of each set of ligands lie approximately perpendicular with respect to each other as well as the mean square plane defined by the metal centers. The tetramer possesses an approximate twofold symmetry normal to the square plane and passing through its midpoint. The mean square plane is distorted, evident from the relative Cd–Cd separations (Cd1–Cd2, 5.880; Cd2–Cd3, 5.892; Cd3–Cd4, 5.841; Cd1–Cd4, 5.857; Cd1–Cd3, 8.261, and Cd2–Cd4, 8.169 Å). The cadmium atoms also deviate from the mean basal plane and remain coplanar within ±0.415 Å. Each cadmium carries three carbon monoxide ligands at terminal positions, giving the metal center an overall octahedral geometry. However, there are substantial departures from the ideal octahedral geometry, due to mainly the formation of chelate bonds by the chloroaryl ligands to each cadmium. The relevant bite angles, 65.4(5), 64.5(5), 65.4(4), and 65.2(5)° for Cd(1), Cd(2), Cd(3), and Cd(4) respectively, are considerably narrower than 90°, expected for ideal geometry. Other angles involving the cis atoms range from 82.9(5) to 105.5(9)° and those involving the trans atoms range from 167.0(9) to 177.3(9)°. These values also indicate considerable distortions in the geometry.

The Cd–C bond lengths involving the carbonyl groups range from 1.80(2) to 1.90(2) Å and have an average value of 1.86 Å. These values may be compared with the sum of the covalent radius of carbon and ionic radius of Cd^{2+} (0.77 + 1.09 = 1.86 Å).[14] However, the Cd–C distances involving the aryl rings are significantly longer with the values lying in the range 2.18(2) to 2.24(2) Å with an average value of 2.19 Å. The Cd–Cl bond lengths vary from 2.514(6) to 2.547(6) Å, and the average value (2.5255 Å) is significantly shorter than the sum of the ionic radii of Cd^{2+} and Cl^- (2.78 Å)[14] which suggests that these bonds are essentially covalent. The Cd–Cl distances in the present complex are also shorter than those found in other six-coordinated anionic species, such as $CdCl_6^{4-}$ (2.588, 2.617, and 2.765 Å).[15] Selected bonding parameters are listed in Supporting Information.[16]

In summary, we described a new method to prepare the novel polymetallic carbonyl compound of cadmium with chloroaryl bridges by a green path using simply *o*-vanillin or *o*-vanillic acid with the cadmium(II) trichloroacetate salt at room temperature and pressure, which could be a green source of carbon monoxide in various catalytic processes. Work in this direction is currently under way in our laboratory.

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13 X-ray structure data: CAD4 diffractometer, ω scans, Mo Kα radiation ($\lambda = 0.71073$ Å), graphite monochromator, $T = 293(2)$ K, structure solution with direct methods (SHELXTL PLUS): G. M. Sheldrick, *Acta Crystallogr., Sect. A* **1990**, *46*, 467; Refinement against F^2 (SHELXL 93) with anisotropic thermal parameters for all non-hydrogen atoms. G. M. Sheldrick, *SHELXL 97-Program for Crystal Structure Refinement*, University of Göttingen, Germany, **1997**. Data collection for **1**: crystal dimension $0.40 \times 0.25 \times 0.15$ mm^3, monoclinic, space group $P2(1)/c$, $a = 10.985(2)$, $b = 18.911(4)$, $c = 23.110(6)$ Å, $\beta = 91.20(3)°$, $V = 4800(2)$ Å^3, $Z = 4$, $D_{calcd} = 1.749$ g cm^{-3}, $\mu = 2.026$ mm^{-1}, $F(000) = 2416$, $2.14 \leq \theta \leq 25.17°$, $-13 \leq h \leq 13$, $0 \leq k \leq 22$, $0 \leq l \leq 27$, 9520 data collected, 8532 unique data ($R_{int} = 0.0432$), 525 refine parameters, GOF (F^2) = 1.046, final R indices ($R_1 = \sum||F_o| - |F_c||/\sum|F_o|$, $wR_2 = [\sum w(F_o^2 - F_c^2)/\sum w(F_0^2)]^{1/2}$): $R_1 = 0.0726$, w$R_2 = 0.2088$, max/min residual electron density 1.388/−2.251 e Å^{-3}. Crystallographic data for the structure reported in this paper have been deposited with the Cambridge Crystallographic Data Center as supplementary publication no. CCDC-185365. Copies of the data can be obtained free of charge on application to CCDC, 12, Union Road, Cambridge, CB2 1EZ, UK (fax: +44 1223 336033); e-mail: deposit@ccdc.cam.ac.uk).

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