



Comments on “Carbonyl releasing Schiff base complex of Fe (III): synthesis, physicochemical characterization, antimicrobial and anticancer studies”

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Abstract. The authors of the title paper (*J. Chem. Sci.* (2020) **132** 44) claim to have synthesized and characterized a carbonyl releasing Schiff base complex of Fe(III) to study its antimicrobial and anticancer properties. A critical analysis of the reported claims reveals that the so-called carbonyl releasing Schiff base complex formulated as containing two carbonyl (CO) ligands bonded to a pentavalent iron, is a dubious material. In this letter to the Editor, it is proved that the title paper is completely erroneous.

Keywords. Carbonyl releasing Schiff base complex; Carbonyl; Iron; Schiff base; Dubious material; Improper characterization.

Dear Editor,

Recently I became aware of the paper¹ by Kupwade and Sawant, published in the *Journal of Chemical Sciences*. The authors claim to have synthesized and characterized a so-called carbonyl releasing Schiff base complex of Fe(III) (hereinafter referred to as **1**) and studied its antimicrobial and anticancer properties. Although the title gives an impression that the paper is on a ferric-Schiff base complex which gives off CO perhaps by heating, a quick survey reveals that **1** is supposed to contain carbonyl (CO) ligands bonded to Fe⁺³. It is well known that the CO ligand stabilizes low positive, zero or even negative formal oxidation states of metal atom². An earlier reported carbonyl of Cd⁺² viz., [Cd(CO)₃(C₆H₃Cl)]₄ has been recently reformulated by Parkin and coworkers as a Re⁺¹ compound³ namely [Re(CO)₃(C₄N₂H₃S)]₄ proving that for some metals like Cd, the CO ligand cannot stabilize +2 state. In the case of Fe, no example of a ferric compound containing one or more CO ligand(s) is reported to date. In order to understand the isolation of a hitherto unknown carbonyl of Fe⁺³, I read the title paper thoroughly. My scrutiny revealed that the presentation of the results do not meet scientific standards and the title paper has fundamental flaws pertaining to the synthesis of **1** and its characterization.

A so-called carbonyl releasing Schiff base complex of Fe⁺³ (1) is a dubious material

In the two-step synthesis of **1** (Scheme 1 in the title paper¹) a Schiff base ligand (LH) is first prepared by the reaction of salicylaldehyde with *p*-nitroaniline. In the second step, CO gas is supposed to have been bubbled into the reaction mixture of the Schiff base ligand (LH) and ferric nitrate in a 2:1 mole ratio in ethanol-water solvent to obtain **1**. The structure of the so-called carbonyl releasing complex **1** is shown as a hexacoordinated compound corresponding to a formula [Fe(CO)₂(L)₂](NO₃)₃ (L = monoanion of Schiff base) with the central metal coordinated to a pair of CO ligands disposed *trans* to each other and a pair of bidentate Schiff base ligands bonded to Fe *via* the phenolate oxygen and the imine nitrogen. The authors refer to **1** as a ferric (Fe⁺³) complex as can be seen in the title and the rest of the paper, without considering that the three nitrate anions and two monoanionic phenolate ligands in the proposed structure of **1** correspond to a pentavalent iron (Fe⁺⁵). The proposed structure with a pentavalent formulation can be ruled out based on the reasoning that passing CO gas into an aqueous ethanolic ferric nitrate solution in the presence of a Schiff base will not result in its oxidation to Fe⁺⁵. It is not clear if authors are aware that pentavalent and tetravalent iron species have been postulated as possible intermediates in biological processes⁴ and in the mechanism of iron-catalyzed oxidations. No example of a structurally characterized

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Fe⁺⁵ compound coordinated to CO ligands is archived in the Cambridge Structural Database⁵ (CSD) or described in standard chemistry textbooks.⁶ There is no compelling proof in the title paper to accept the Fe(V) formulation, as shown below.

The dubious nature of **1** can be evidenced from the procedure employed for the production of CO which is as follows: “The gaseous CO ligand was produced in separate flask by the reaction of conc. HCl with calcium carbonate and zinc powder mixture...”, This is not only unusual but also incorrect because the reaction of HCl with a mixture of CaCO₃ and Zn gives a mixture of carbon dioxide (CO₂) and hydrogen (H₂) but not any CO.

Under the heading, ‘FTIR spectrum of Schiff base and CORM complex’ authors reported, “Signals at 1760 and 1822 cm⁻¹ elaborates the presence CO groups over Fe(III) metal ion in the complex.” This claim can be dismissed as inappropriate since the reported IR spectrum does not show any signals at 1760 and 1822 cm⁻¹ and authors assign a fictitious signal at 1824 cm⁻¹ (in Table 2¹) for out of plane nitro groups. Regrettably, all the infrared spectral assignments and the discussion of the noisy UV-Vis spectrum of **1** are incorrect and unacceptable.

The reported X-ray powder pattern of **1** has serious issues, as shown below. It is not clear what the authors mean by “Octahedral rhombohedral crystal symmetry” which is mentioned in the X-ray powder pattern. While discussing the result of their powder pattern, authors reported, “...The XRD data is determined using miller indices of pattern, Scherer’s formula and packing of planes and it was matched with octahedral Fe(III) data in JCPDS card no. 85-3854...” Since the so-called carbonyl releasing Fe(III) complex is supposed to be a new material, it is not clear as to why its powder pattern was matched with a fictitious JCPDS card to determine the lattice constants *a* and *b* as 3.251 and 5.272 Å respectively. In a recent Pub Peer post,⁷ Le Bail who is an authority on powder diffraction⁸ commented the following “More than strange, the powder diffraction pattern shown in this paper and said to correspond to a Fe(III) complex is exactly the same as a ZnO powder pattern: unexplainable...” showing that the powder pattern in the title paper has nothing to do with a Fe(III) complex but is that of the hexagonal polymorph of zinc oxide. What is worrisome is that the powder pattern corresponds to a phase

pure zinc oxide and not to any Fe(III) complex as claimed by the authors. The ZnO can perhaps explain the strange looking infrared spectrum of **1**.

In view of the several inconsistencies, the following claim “The TEM results were matched with XRD data and proved the chelate octahedral nature of complex with the crystalline state for good water solubility and further biocompatibility...” can be summarily dismissed. Although the authors believe that their so-called CORM (carbonyl releasing Fe(III) complex) has potential biomedical applications, I wish to mention that due to the improper characterization of **1**, its antimicrobial and anticancer studies have no scientific merit.

In summary, it is proved that a so-called carbonyl releasing Schiff base complex of Fe(III) is a dubious material and the title paper is completely erroneous.

Declarations

Competing interest The author declares that he has no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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