Oxalate production via oxidation of ascorbate rather than reduction of carbon dioxide

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In the previous publication, some of us reported the conversion of a copper(I) complex to a copper(II) oxalate complex, and claimed that this conversion involved a reduction of CO2 to oxalate (C2O42−). Herein, we show that the oxalate is produced not by reduction of CO2, but by reaction of ascorbate with oxygen. We also present new results that explain in a more comprehensive way the behaviour of these copper compounds under O2 and CO2.

Selective reduction of carbon dioxide to C2O2 compounds using homogeneous metal complexes is a challenging transformation. Only a limited number of examples have been reported over the past decades1–12. In contrast, there has been a vast increase in reported catalysts for selective CO2 reduction to C1 compounds13–15. Among the examples reported for the reductive coupling of CO2 to oxalate is a dinuclear Cu complex introduced by some of us in 2014 (ref. 16). The in situ generated Cu(I) complex [Cu2(m-xpt)2](PF6)2 (3) formed by reduction of the Cu(II) precursor 1 with sodium ascorbate generated an oxalate-bridged dinuclear complex (4), proposed to occur via reductive coupling of atmospheric CO2 (Fig. 1). Release of the oxalate by addition of mineral acids was described, potentially enabling stepwise conversion of CO2 into oxalic acid using sodium ascorbate as a comparatively mild reductant.

Interestingly, oxidation of ascorbic acid by transition metal compounds, especially those of copper, has been well-known for more than a century17,18. Since then, the reaction mechanisms for such oxidations have been intensely studied18–22. More specifically, oxidative degradation of ascorbic acid by (a) inorganic oxidants (sodium periodate23, sodium hypoiodite24); (b) oxygen25,26; and (c) O2 in the presence of Gd27–29, Co30, Pd30, Pt31, Cd30, Fe31, or Cu32 compounds is reported to yield oxalate as a degradation product (see Supplementary Fig. 21 for a typical reaction sequence).

We now report that the true origin of the oxalate in the communication published in 2014 is not CO2, as it was described, but oxidative degradation of sodium ascorbate. A first hint towards the oxidative degradation pathway as the origin of oxalate was obtained when treatment of the in situ generated Cu(I) complex [Cu2(m-xpt)2](PF6)2 (3), formed via reaction of the Cu(II) precursor 1 with sodium ascorbate in DMF, with CO2 over 6 days did not result in the previously described colour change from yellow to green (Supplementary Fig. 1) and no Cu(II) species was detected by UV/Vis spectroscopy (Supplementary Fig. 2). However, after introduction of air, oxidation of the Cu(I) complex 3 was observed and followed by UV/Vis spectroscopy over 189 h, resembling the UV/Vis spectra reported in the previous publication.

The product obtained from this reaction after slow evaporation of the solvent was identical to the reported oxalate complex 4, as evident from the IR spectrum (Supplementary Fig. 3).

Since the reaction seemed to require air for the formation of oxalate, we suggested that oxidation of the ascorbate might be the true origin of the oxalate. Therefore, the previously published results might have eventuated from oxygen contamination of the reaction mixtures utilised for the labelling studies and the UV/Vis spectroscopic study.

To test this hypothesis, we prepared the Cu(I) complex 3 in situ using sodium ascorbate, and exposed it to oxygen in the absence of air and CO2. Indeed, oxidation of the Cu(I) complex 3 in the presence of O2 occurred within a few minutes, as evidenced by a characteristic colour change from yellow to green (Supplementary Fig. 5) and after 5 days of reaction time, a yellow to green solid was obtained after removal of the solvent. As suspected, the solid product was identical to that obtained via the reaction of the in situ generated Cu(I) complex 3 with air, as evident from X-ray analysis and FTIR spectroscopy (see spectra in Fig. 2).

Complex 4 was even obtained from a mixture of Cu(II) complex 1 and DHA in air, demonstrating that Cu(I) is not required for oxalate formation.

The Cu(I) complex [Cu2(m-xpt)2]2+ can also be prepared without ascorbate or dehydroascorbic acid, for example, by...
reaction of Cu(BF$_4$)$_2$ with Cu foil in DMF in the presence of m-xpt. This yellow solution of [Cu$_2$(m-xpt)$_2$][(BF$_4$)$_2$] (3a, identical to 3 except for the counterion) (a) does not react with CO$_2$; (b) reacts with air to produce the new trinuclear Cu(II) carbonate complex [Cu$_3$(m-xpt)$_3$(μ$_3$-CO$_3$)](BF$_4$)$_4$ (6); and (c) can be converted to the oxalate complex [Cu$_2$(m-xpt)$_2$(μ$_2$-C$_2$O$_4$)][BF$_4$]$_2$ (4b) by reaction with air or O$_2$, but only if DHA is added. These observations are also in accordance with ascorbate being the source of oxalate. The structures of 6 and 4b were determined by X-ray analysis (see Supplementary Fig. 13).

In the previous publication, an isotope labelling experiment was conducted by treating in situ generated 3 with $^{13}$CO$_2$. In mass spectrometry experiments performed on 4 at that time, we did not observe signals attributable to oxalate-containing product ions; however, its FTIR spectrum appeared to show a shift of $\Delta \tilde{\nu}_{\text{CO}} = -19$ cm$^{-1}$. Since this shift was only half the expected magnitude, we re-performed the labelling studies. In the new experiments, treatment of in situ generated 3 with $^{13}$CO$_2$–O$_2$ (1:1) produced only unlabelled 4, whose ESI-MS shows a monoisotopic ion at 1147.1321 amu for [Cu$_2$(m-xpt)$_2$(μ$_2$-C$_2$O$_4$)][PF$_6$]$^+$ (see Supplementary Fig. 9). The $^{13}$C-labelled oxalate complex 4, $^{13}$C$_2$ was obtained, for reference, by reaction of the starting complex 1 with (Bu$_4$N)$_2$(13C$_2$O$_4$); monoisotopic ion 1149.1373 amu. This analysis clearly demonstrates that oxalate does not arise from CO$_2$. 

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**Fig. 1** Reactions of Cu(II) complex 1 and the Cu(I) complex 3 obtained by reduction of 1 with ascorbate. For the formation of oxalate complex 4 from 3, CO$_2$ was previously reported to be required. We show here that the reaction requires ascorbate or dehydroascorbic acid (DHA), and oxygen. If ascorbate and DHA are absent, oxidation of 3 in air produces 6. All reactions were conducted in DMF, except for the removal of oxalate from 4 (Note: 1, 3, and 4 represent the same compounds as in ref. 16).

**Fig. 2** Formation of the oxalate complex 4 from 3 requires O$_2$ and does not require CO$_2$. FTIR spectra for the products obtained when 3 (prepared in situ from 1 and ascorbate) was exposed to air (grey) or pure O$_2$ (green) are identical (details are given in the ESI).
reaction of in situ generated absorption is caused by co-crystallized DMF in bound oxalate is 1639 cm$^{-1}$; the spectra in Supplementary Fig. 7 suggest that different samples of 4 may show varying absorption in the 1670–1640 cm$^{-1}$ region. This variability may have led to the incorrect assignment of an apparent 13C shift in the previous work.

Due to this complexity of the IR spectra, we searched for additional experimental evidence for the formation of oxalate from the reaction under O$_2$ atmosphere. We repeated the previously described oxalate removal by treatment with aqueous HNO$_3$ (ref. 16), but we could not detect the expected H$_2$C$_2$O$_4$ by 13C NMR spectroscopy. Therefore, we adapted a procedure which was utilised for the isolation of Na$_2$C$_2$O$_4$ from similar Cu oxalate complexes. We used this procedure to isolate Na$_2$C$_2$O$_4$ (verified by 13C NMR spectroscopy), from samples of 4 obtained by reaction of in situ generated 3 with (a) air (i.e. O$_2$ + CO$_2$; Supplementary Fig. 18), and (b) pure O$_2$ (i.e. without CO$_2$; Supplementary Fig. 16). In the latter case, the isolation of Na$_2$C$_2$O$_4$ from 4 was conducted under argon, so the isolated oxalate could not be formed by any reaction requiring CO$_2$.

In summary, we have demonstrated that the Cu complex reported in the previous communication does not form oxalate via CO$_2$ reduction. Instead, oxalate forms by oxidative degradation of ascorbate. This was finally evidenced by the reaction conducted under an atmosphere of O$_2$, giving rise to the same oxalate complex described earlier (ref.19) from which sodium oxalate was removed and identified by NMR spectroscopy. In addition, the same product was obtained from reactions of the Cu(I) complex [Cu$_2$(m-xpt)$_2$]$^{2+}$ with O$_2$ or air in the presence of DHA. In experiments with [Cu$_2$(m-xpt)$_2$]$^{2+}$ under $^{13}$CO$_2$ + O$_2$, $^{13}$C was not incorporated into the oxalate product. In contrast, a new trinuclear Cu(II) carbonate complex, [Cu$_3$(m-xpt)$_4$(μ-CO$_2$)$_4$]$^{4+}$, has been isolated, when [Cu$_2$(m-xpt)$_2$]$^{2+}$ was treated with CO$_2$ and O$_2$ in the absence of sodium ascorbate or DHA. Since reproducibility is not always given for challenging transformations, such as the reductive coupling of CO$_2$, this report clearly highlights the importance of further mechanistic investigations on previously published systems.

### Data availability

Accession codes: The X-ray crystallographic data for structures reported in this article have been deposited at the Cambridge Crystallographic Data Centre (CCDC), under deposition numbers CCDC 1976241 (4b) and 1976240 (6). These data can be obtained free of charge from the Cambridge Crystallographic Data Centre via https://www.ccdc.cam.ac.uk/structures/. Other data are available from the authors.

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Author contributions

F.K., M.M., D.B.C., and U.R.P. performed the synthetic work, and conducted the spectroscopic analyses. F.R.F. performed X-ray analysis. F.K., M.M., M.B., and A.W.M. contributed to writing.

Competing interests

The authors declare no competing interests.

Additional information

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