

Experimental evidence of the disproportionation equilibrium in copper mixed-valence complexes

Crivelli, Irma G.

Andrade, Carlos

Francois, Angélica

Boys, Daphne

Haberland, Annamaria

Segura, Rodrigo

María Leiva, Ana

Loeb, Bárbara

Experimental evidence for a dismutation equilibrium in the mixed-valence (MV) $[M^{n+} - M^{(n+1)+}]$ system type has been elusive and its existence can be established only when the oxidation-reduction processes involved are reversible. Previous research in the field of binuclear $Cu(II)-Cu(II)$, $Cu(I)-Cu(I)$ and the related MV $Cu(II)-Cu(I)$ complexes allowed us to obtain electrochemical evidence for the disproportionation equilibrium in some of these systems. In this communication we report discuss experiments with $[(RCOO)_2Cu(II)-Cu(I)(OOCR)_2]^-$ ($R = CH_3, Ph$) type MV complexes that give direct non-electrochemical experimental evidence for the presence in solution of the disproportion equilibrium: $2[(R-COO)_2Cu(II)-Cu(I)(OOC-R)_2]^- \rightleftharpoons (R-COO)_4Cu_2(II) + [(RCOO)_4Cu(I)_2]^{2-}$ It was possible to isolate the different components of the disproportionation equilibrium by varying temperature and solvent conditions. To our knowledge, this is the first non-electrochemical experimental evidence of this equilibrium fo