Supplementary Information

Solvation of Copper(II), Zinc(II) and Lead(II) in Monoethanolamine Solutions Attained via Leaching of Microwave-Assisted-Roasted Sulfidic Tailings

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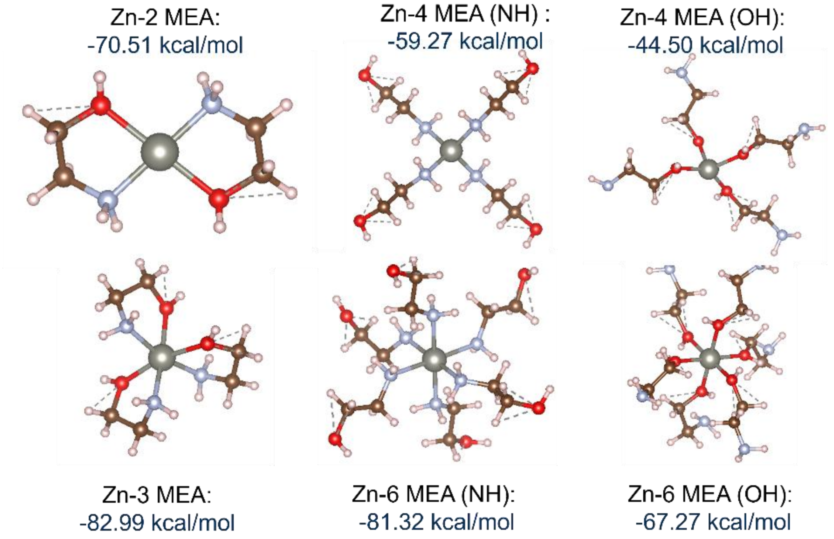
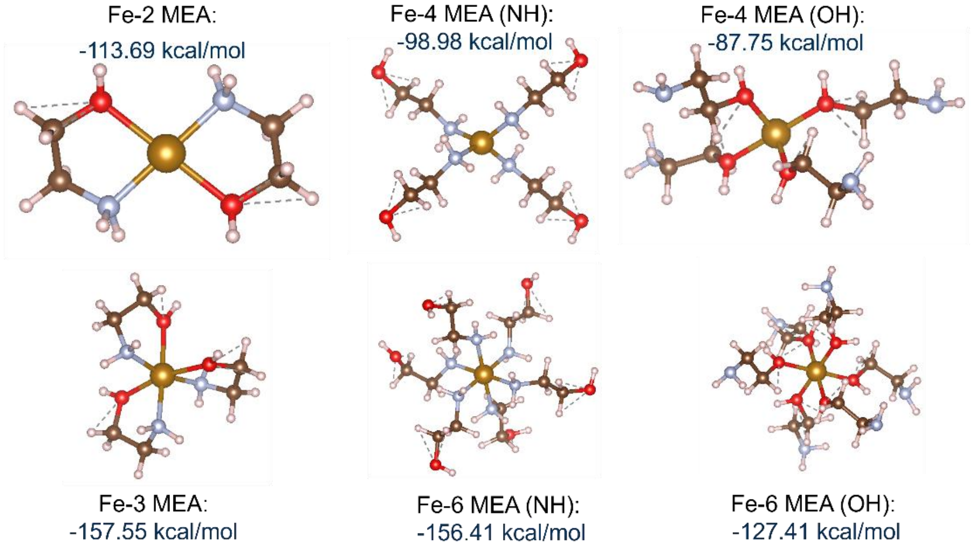
Zn-MEA complex



Octahedral Zn-MEA (3,6) complexes show higher stability, when compared to tetrahedral complexes.

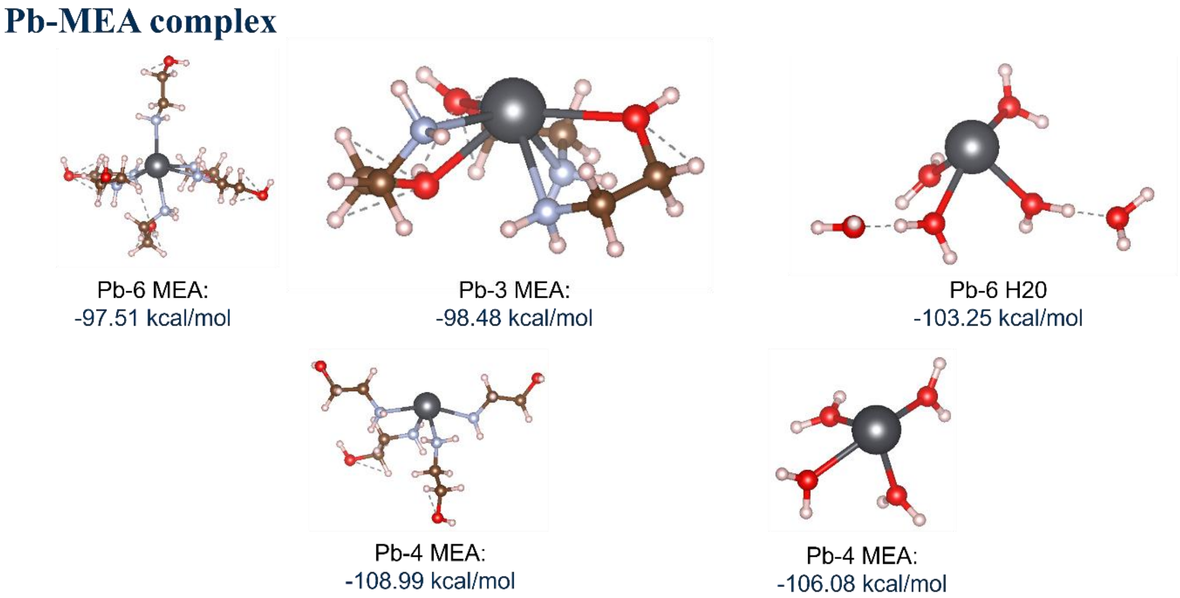
Figure SI-1: Different tetrahedral (top) and octahedral (bottom) Zn-MEA configurations considered in this study, to determine the stable Zn-MEA complexes. The possibility of MEAs coordinating with metal cation either via hydroxyl or amine groups and either as monodentate or bidentate ligands were considered. DFT binding energies of octahedral amine coordinated MEA-Metal complexes: Zn-6 MEA (NH) and amine/hydroxyl coordinated bidentate: Zn-3 MEA complexes showed higher binding affinities (lower binding energies) and stabilities compared to the tetrahedral (top) complexes or hydroxyl coordinated Zn-6 MEA (OH) complexes (bottom right).

Fe-MEA-Complex



Octahedral Fe-MEA (3,6) complexes show higher stability, when compared to tetrahedral complexes.

Figure SI-2*:* Different tetrahedral (top) and octahedral (bottom) Fe-MEA configurations considered in this study, to determine the stable Fe-MEA complexes. The possibility of MEAs coordinating with metal cation either via hydroxyl or amine groups and either as monodentate or bidentate ligands were considered. DFT binding energies of octahedral amine coordinated MEA-Metal complexes: Fe-6 MEA (NH) and amine/hydroxyl coordinated bidentate: Fe-3 MEA complexes showed higher binding affinities (lower binding energies) and stabilities compared to the tetrahedral (top) complexes or hydroxyl coordinated Fe-6 MEA (OH) complexes (bottom right).



Tetrahedral Pb-MEA (4) complexes show the higher stability, when compared to octahedral complexes, which upon optimization resulted in highly distorted geometries.

Figure SI-3*:* Different tetrahedral and octahedral Pb-MEA configurations considered in this study, to determine the stable Pb-MEA complexes. The possibility of MEAs coordinating with metal cation either via hydroxyl or amine groups and either as monodentate or bidentate ligands were considered. DFT binding energies of tetrahedral octahedral amine coordinated MEA-Metal complexes: Pb-4 MEA showed higher binding affinities and stabilities compared to other structures considered. Pb-MEA complexes, however, show higher affinity towards tetrahedral complexes with 4-MEA fragments, wherein Pb-6MEA and Pb-6H_2O complexes show high structural distortions and/or cleavage of the metal-fragment coordination bond upon DFT optimization (see top right image).

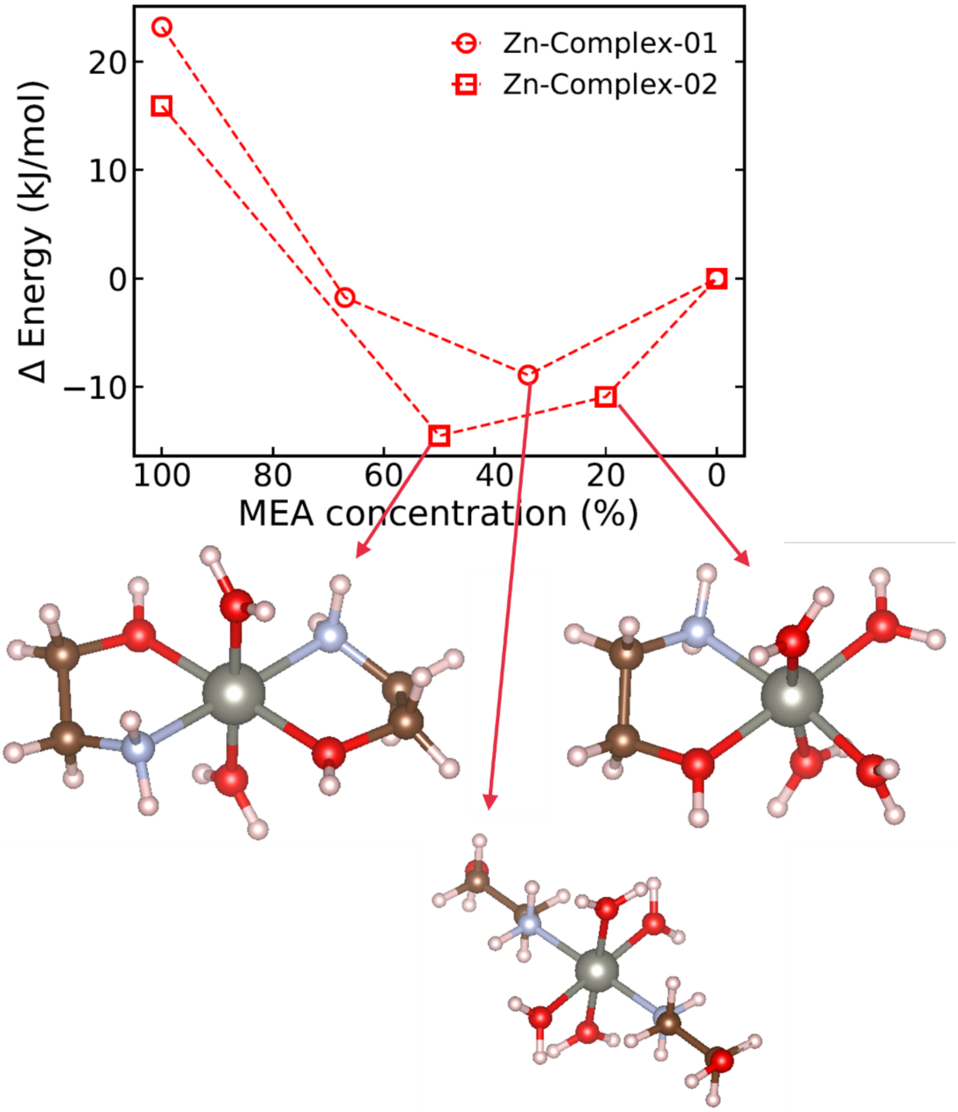


Figure SI-4: ΔE_{BB} values for Zn-MEA+water metal cation complexes as a function of the MEA concentration in water. Complex1 represents monodentate complexes and Complex 2 represents bidentate complexes.

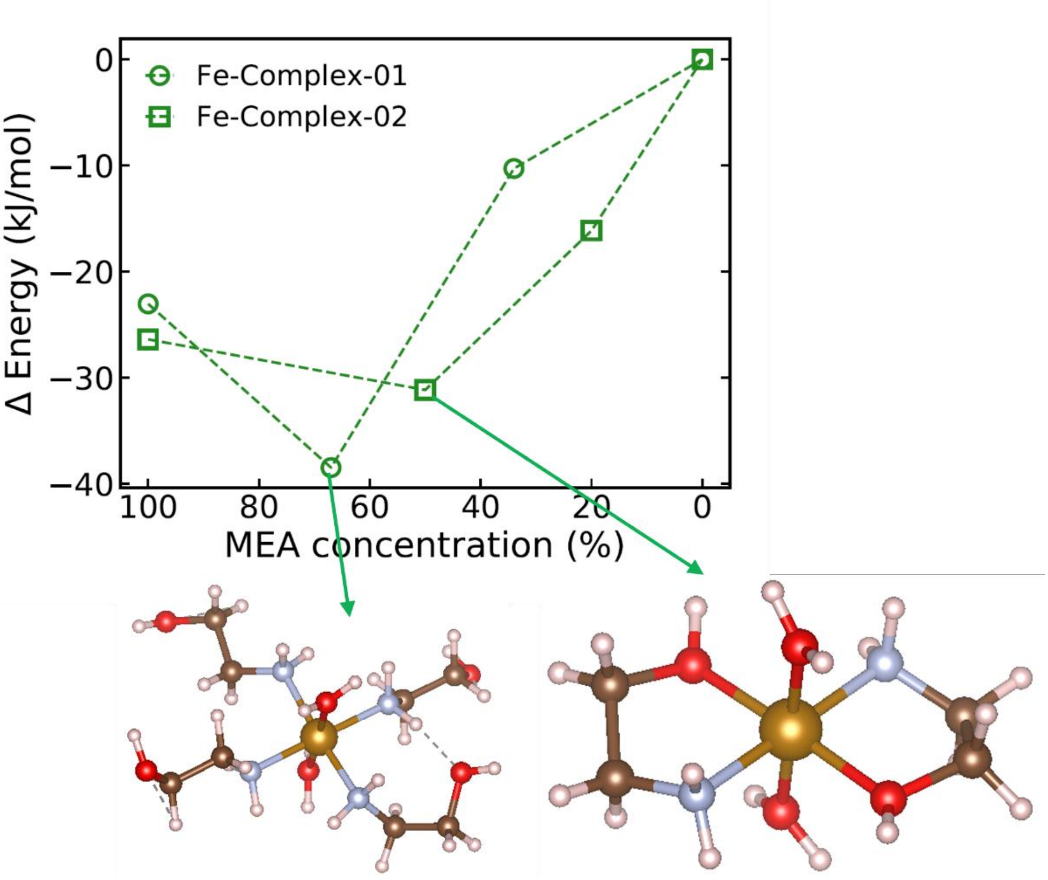


Figure SI-5: ΔE_{BB} values for Fe-MEA+water metal cation complexes as a function of the MEA concentration in water. Complex1 represents monodentate complexes and Complex 2 represents bidentate complexes.

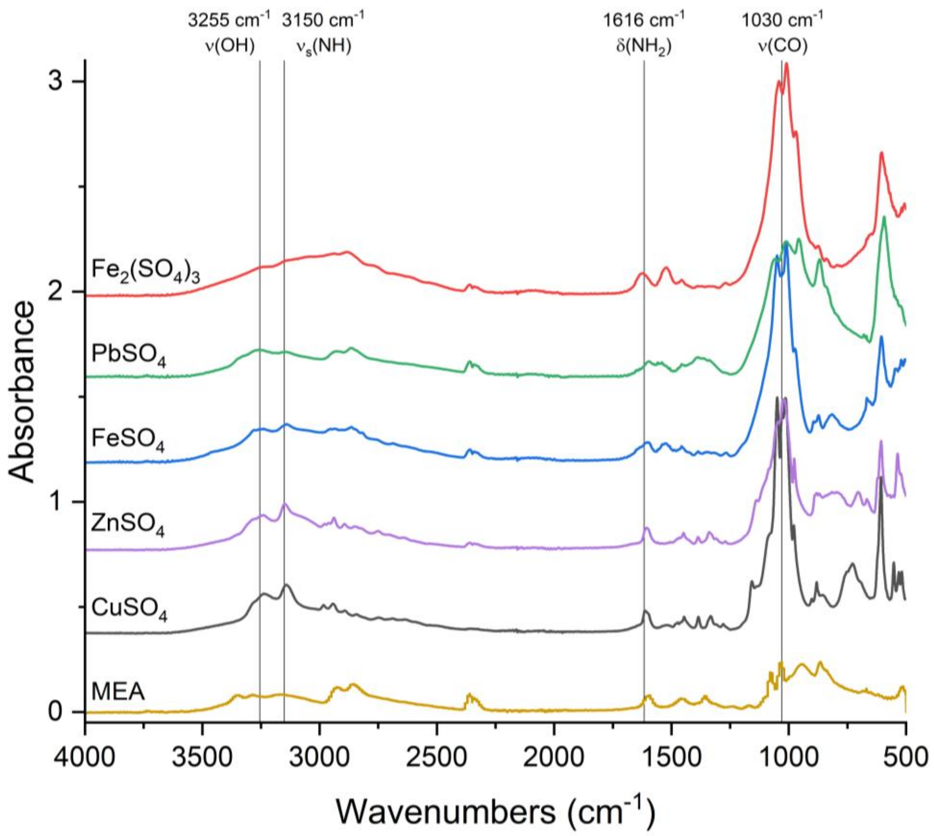


Figure SI-6: FT-IR absorbance spectra of pure MEA and of metal sulphate salts with MEA addition in a 2:1 MEA:metal molar ratio. The superimposed peak positions are positions of the $Cu(MEA)_3SO_4$ complex, reported by Brannon et al.[1]

Figure SI-6 shows the FT-IR spectrum of pure MEA and the spectra of dehydrated sulphate salts which were wetted by MEA according to a molar ratio MEA:metal of 2 (additional MEA gave in many cases a wet material indicating the presence of non-complexed MEA). To the spectra the peak positions of the $CuSO_4$ – MEA complex $Cu(MEA)_3SO_4$ as reported by Brannon et al.[1] were added. In particular the OH and CO stretch, the symmetric NH stretch and the NH_2 in-plane bending are shown and do coincide with peaks of the here recorded $CuSO_4$ + MEA spectrum. The spectrum of $ZnSO_4$+MEA is similar to that of the $CuSO_4$-MEA complex, indicating a similar coordination. Furthermore, the same observation can be made for the $FeSO_4$+MEA complex, although some divergence in the regions 3000-2700 cm^{-1} and 1500-1250 cm^{-1} can be observed. The spectrum of $PbSO_4$-MEA still shows the presence of the OH and NH stretching peaks, although these are less intense and the fingerprint region 1500-500 cm^{-1} differs quite significantly from the previous three complexes. This could indeed indicate and coincide with the different coordination number of MEA to Pb(II) in respect to Cu(II), Zn(II) and Fe(II), as discussed in the manuscript and predicted through DFT modelling. From FT-IR it can be derived that MEA coordination to Fe(III) sulphate ($Fe_2(SO_4)_3$) differs significantly from the bivalent metals.

Table SI-1: Wiberg bond order variations for Zn-MEA complex.

Zn-MEA complex, Wiberg bond order variations for Complex-1; monodentate coordination					
Complex	% (MEA)	Zn-N; N of MEA*	Zn-O; O of MEA*	Zn-O; O of H_2O*	Net BO*
$[Zn(MEA)_6]^{2+}$	100	0.143	--	--	0.858
$[Zn(MEA)_4(H_2O)_2]^{2+}$	66	0.174	--	0.155	1.006
$[Zn(MEA)_2(H_2O)_4]^{2+}$	33	0.195	--	0.165	1.056
$[Zn(H_2O)_6]^{2+}$	0	--	--	0.174	1.044
Zn-MEA complex, Wiberg bond order variations for Complex-2; bidentate coordination					
Complex	% (MEA)	Zn-N; N of MEA*	Zn-O; O of MEA*	Zn-O; O of H_2O*	Net BO*
$[Zn(MEA)_3]^{2+}$	100	0.161	0.154	--	0.945
$[Zn(MEA)_2(H_2O)_2]^{2+}$	50	0.209	0.169	0.168	1.094
$[Zn(MEA)_1(H_2O)_4]^{2+}$	20	0.205	0.166	0.171	1.057
$[Zn(H_2O)_6]^{2+}$	0	--	--	0.174	1.044

*Zn-N; N of MEA represents the bond order between metal atom and nitrogen atoms of MEA molecule, Zn-O; O of MEA represents the bond order between metal atom and oxygen atoms of MEA molecule, Zn-O; O of H_2O represents the bond order between metal atom and oxygen atoms of water molecule. Net BO is the net bond order of the metal atom in the complex

Table SI-2: Wiberg bond order variations for Fe-MEA complex.

Fe-MEA complex, Wiberg bond order variations for Complex-1; monodentate coordination					
Complex	% (MEA)	Zn-N; N of MEA*	Zn-O; O of MEA*	Zn-O; O of H_2O*	Net BO*
$[Fe(MEA)_6]^{2+}$	100	0.385	--		2.310
$[Fe(MEA)_4(H_2O)_2]^{2+}$	66	0.428	--	0.358	2.428
$[Fe(MEA)_2(H_2O)_4]^{2+}$	33	0.422	--	0.354	2.260
$[Fe(H_2O)_6]^{2+}$	0	--	--	0.365	2.190
Fe-MEA complex, Wiberg bond order variations for Complex-2; bidentate coordination					
Complex	% (MEA)	Zn-N; N of MEA*	Zn-O; O of MEA*	Zn-O; O of H_2O*	Net BO*
$[Fe(MEA)_3]^{2+}$	100	0.431	0.355	--	2.358
$[Fe(MEA)_2(H_2O)_2]^{2+}$	50	0.439	0.367	0.363	2.349
$[Fe(MEA)_1(H_2O)_4]^{2+}$	20	0.430	0.365	0.363	2.247
$[Fe(H_2O)_6]^{2+}$	0	--	--	0.365	2.190

*Fe-N; N of MEA represents the bond order between metal atom and nitrogen atoms of MEA molecule, Fe-O; O of MEA represents the bond order between metal atom and oxygen atoms of MEA molecule, Fe-O; O of H_2O represents the bond order between metal atom and oxygen atoms of water molecule. Net BO is the net bond order of the metal atom in the complex.

REFERENCES

1. D. G. Brannon, R. H. Morrison, J. L. Hall, G. L. Humphrey and D. N. Zimmerman, *Journal of Inorganic and Nuclear Chemistry*, 1971, **33**, 981-990. DOI: 10.1016/0022-1902(71)80164-1.