Is copper(I) hard or soft? A density functional study of mixed ligand complexes†

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Fully optimized structures of three- and four-coordinated Ni(0), Cu(I) and Zn(II) complexes with varied combination of hard (H_2O or H_3N) and soft (H_2S, H_3P) ligands were computed using density functional theory (DFT). Frequency calculations were carried out to ascertain that the structures were true minima. In the case of Cu(I) and Zn(II), the heat of formation (HOF) values are smaller with larger number of soft ligands. The increase in the HOF on replacing a soft ligand with a hard ligand is less for Cu(I) than for Zn(II). The corresponding HOF is negative for Ni(0) which is not stable with a complement of four hard ligands. The calculated chemical hardness parameters based on vertical ionization potentials clearly indicate the preference of four hard ligands for Zn(II) and four soft ligands for Ni(0). Significantly, the maximum chemical hardness was computed for Cu(I) complex $[Cu(PH_3)_3(NH_3)]^+$, a combination of three soft and one hard ligand. The conclusions derived from absolute hardness data computed for the complexes closely parallel the experimentally observed stability of Cu(I) with an optimum number of hard and soft ligands in its coordination sphere in solution.

1 Introduction

Copper(I) complexes are extensively studied. Their presence in biological systems is ubiquitous, for they carry out essential functions like electron transfer,[1] oxygen activation or oxygen transport.[2] Their vast utility in the laboratory, as catalysts responsible for cyclopropanation,[3] addition or oxidation reactions adds to the interest.[4] However, the active species responsible for these functions often remains an unknown entity.

In this milieu, the principle of hard and soft acids and bases (HSAB) has been an extremely good guiding principle for the inorganic chemist.[5] Copper(I) has been classified as a soft cation.[6] However, the ability of copper(I) to bind hard or soft donors and the different reactivities exhibited by copper(I) complexes has raised some questions about the nature of copper(I).[7] It has been observed that the stability of a copper(I) complex coordinated to a mixture of hard and soft donors is in fact greater than a complex with only soft donors.[8] Is copper(I) hard or soft? Do the presence of soft ligands around copper(I) symbiotically increase the preference of copper(I) for soft ligands as suggested by Pearson?[6] Several aspects of copper(I) chemistry are enigmatic and this is reflected in a recent paper by Nakamura entitled "Wherefore art thou copper?"[9]

The concept of HSAB has recently gained further utility and popularity due to the definition of absolute hardness η and absolute electronegativity χ which is the negative of the electronic chemical potential.[10] The quantitative nature of η has definitely made the concept more appealing. Apart from the new definition of absolute hardness, density functional theory (DFT) has also suggested the principle of maximum hardness.[11] It implies that a molecule will be most stable when it is hardest, *i.e.* when the HOMO–LUMO gap is maximised in a molecule.[12] This principle of maximum hardness has also been extensively investigated theoretically and its verification has been sought through the analysis of existing data.[13] However, the quantitative picture of hardness cannot help in understanding copper(I) unless ionization potential (IP) and electron affinity (EA) data are available for all molecules. Experimental data on the stability and reactivity of mixed ligand complexes are difficult to come by. Electrospray mass spectrometry has been used elegantly by Deng and Kebarle to estimate the bond energies of CuL_2 and $CuLL'$ complexes and compare them with corresponding Ag(I) and Li(I) complexes.[14] Large deviations from the expected bond energies of copper(I) complexes with NH_3, Me_2S and histidine were seen as evidences for the soft nature of copper(I).[14]

In view of the difficulties encountered in the experimental determination of mixed ligand complexes, a theoretical study based on Density Functional theory utilizing the Gaussian suite of packages has been carried out with hard (H_2O/NH_3) and soft (H_2S/PH_3) ligands in the coordination sphere of copper(I). The heats of formation of the four- and three-coordinated complexes from which they must be formed have been calculated. Absolute hardness values have been calculated from vertical ionisation potentials and electron affinities

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† Electronic supplementary information (ESI) available: Tables S1–S7: Total energy (E) (zero point energy corrected), ionization potential (IP) and electron affinity (EA) of Ni(0), Cu(I) and Zn(II) complexes of H_2S, H_2O, PH_3 and NH_3. See DOI: 10.1039/b618494b

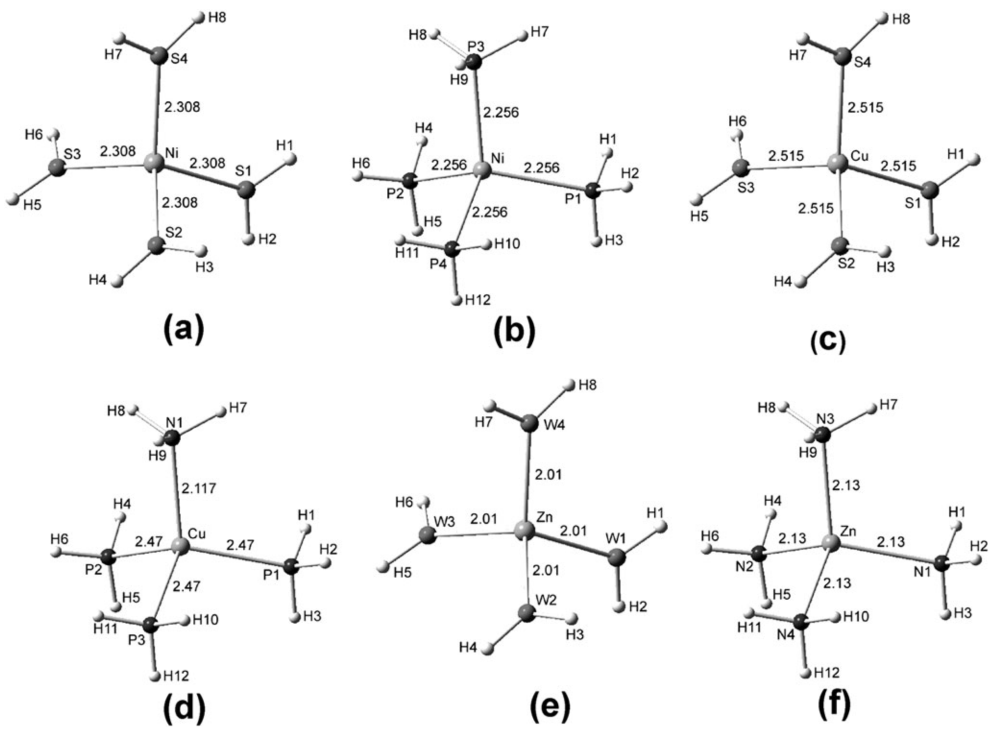

Fig. 1 Geometry optimized structures of (a) NiS_4, (b) NiP_4, (c) CuS_4, (d) CuP_3N, (e) ZnW_4 and (f) ZnN_4.

and the values have been compared with the relative hardness calculated from the bond dissociation energies. The possibility of symbiosis in the hardness of complexes and the principle of maximum hardness have been examined. The corresponding complexes of Zn(II) and Ni(0) have also been studied. Zinc complexes provide an example of an isoelectronic hard cation and Ni(0) complexes are the analogous soft species.

2 Computational methods

DFT calculations were performed using the Gaussian 03 program.[15] All structures were fully optimised using Becke's three-parameter hybrid functional[16] (B3LYP) as implemented in Gaussian 03. All atoms were described using the LANL2DZ basis set as implemented in Gaussian 03. Additional single-point energies were computed at the B3LYP geometries to calculate the ionisation potential (IP) and electron affinity (EA) in order to calculate the chemical hardness. To probe the basis set dependence of the calculated hardness, IP and EA were calculated for a series of four-coordinated Cu(I) complexes with and without polarization functions *i.e.* 6-31G(d,p) and 6-31G, respectively, on PH_3 and NH_3 ligands. Since the hardness of the species increased only marginally and in a uniform fashion, the trends are likely to be the same. The hardness was not recalculated for all species. Frequency calculations were carried out to confirm the minimum energy geometry obtained by the geometry optimisation. Total energy (E) (zero point energy corrected), ionization potential (IP) and electron affinity (EA) values of Ni(0), Cu(I) and Zn(II) complexes of H_2S, H_2O, PH_3 and NH_3 are given in the ESI, Tables S1–S7.†

3 Results

3.1 Geometry optimization

In this study H_2S (S). H_2O (W), PH_3 (P) and NH_3 (N) ligands have been used as probe ligands (ESI,† Table S1). Here, we have restricted the study to two groups of metal complexes involving the combination of ligands H_2S and H_2O, and ligands PH_3 and NH_3 in different ratios. The three- and four-coordinated complexes of metal ions were optimized without symmetry constraints. The geometry optimizations have been carried out for all combinations of hard (H_2O and NH_3) and soft (H_2S and PH_3) ligands for Cu(I). Geometry optimizations have also been carried out for Zn(II) and Ni(0) complexes which are isoelectronic with the corresponding complexes of Cu(I). The minimum energy geometry in each case was confirmed by the frequency calculation. To simplify the visualization, we have used symmetry descriptions that include the metal and the heavy atoms involved. As a representative example, the most stable (*vide infra*) complex in each case is depicted in Fig. 1.

3.1.1 Ni(0) complexes. Full geometry optimization was carried out for NiL_3 and NiL_4 (L = H_2S, H_2O, NH_3 and PH_3) complexes with various combinations of hard and soft ligands. The NiS_4 and NiS_3 complexes optimized close to the tetrahedral and trigonal geometry, respectively (Table 1). Addition of one water molecule in NiS_2W leads to significant shortening of the Ni–S bond distance.

The NiP_4 optimized to give a perfect tetrahedral geometry (Table 2). The NiP_3N and NiN_3P complexes optimized to give a symmetrical complex with a C_3 axis. The NiP_2N_2 complex

Table 1 Selected bond distances (Å) and bond angles (°) of three- and four-coordinated Ni(0) complexes of H_2S and H_2O

	System[a]		
	NiS_4	NiS_3	NiS_2W
Ni–S	2.308	2.235	2.197
Ni–O	—	—	2.098
S–Ni–S	104.08, 116.94, 117.07, 107.04, 105.98, 104.86	120.14, 119.20, 120.34	133.05
O–Ni–S	—	—	112.84

[a] Ni = Ni(0), S = H_2S, W = H_2O.

optimized to give a complex with a C_2 axis. A noticeable fact is that the N–Ni–N angle (99.64°) is smaller than the P–Ni–P angle (107.59°) and P–Ni–N angle (112.42°). Identical observations were made in NiPN_3. The NiN_4 complex did not optimize to a stable structure. The three-coordinated Ni(0) complexes of PH_3 and NH_3 ligands have also been subjected to optimization. The optimized structural parameters are summarized in Table 2. The NiP_3, NiP_2N and NiPN_2 complexes optimized to give trigonal planar geometry around the metal center. The NiN_3 complex does not optimize to a stable structure.

3.1.2 Cu(I) complexes. Three- and four-coordinated Cu (Cu = Cu(I)) complexes of hard and soft ligands were optimized. The CuS_4 and CuW_4 complexes were optimized in a tetrahedral geometry. In the mixed ligands complexes CuS_2W_2 and CuSW_3, the average O–Cu–O angles are substantially smaller than the S–Cu–S and S–Cu–O angles. The first group of three-coordinated complexes (CuS_3, CuS_2W, CuSW_2 and CuW_3) optimized close to the triangular geometry. Details are given in Table 3. The second group of complexes with PH_3 and NH_3 ligands was also subjected to full optimization. Considering only the heavy atoms, three-coordinated CuP_3 and CuN_3 complexes optimized to give symmetrical trigonal structures (Table 4). Similarly the geometries of the CuP_4 and CuN_4 were optimized to be tetrahedral. Interestingly, optimized structures of all the three- and four-coordinated complexes with different combinations of hard (N and W) and soft ligands (P and S) were obtained for Cu(I).

3.1.3 Zn(II) complexes. In the case of Zn^{2+} complexes, the three-coordinated ZnW_3 complex (Zn = Zn^{2+}) optimized to give the symmetrical, trigonal structure but ZnS_3 complex optimized to a distorted geometry (Table 5) with three different S–Zn–S angles. The ZnWS_2 complex optimized to give the C_{2v} geometry considering only the heavy atoms, but ZnW_2S is not symmetrical and this can be seen from Table 5. The four-coordinated ZnW_4 and ZnS_4 complexes optimized to give distorted tetrahedral structures. The other four-coordinated ZnS_3W and ZnSW_3 complexes optimized to give distorted structures. The ZnW_2S_2 complex optimized to give a symmetrical structure. The second group complexes (PH_3 and NH_3 complex of Zn(II)) are also subjected to full optimization and give quite symmetrical complexes (Table 6).

3.2 Heats of reaction

Heats of reaction are computed for the substitution reaction as well as for the overall complex formation in tetra-coordinated complexes. The heat of reaction values as defined in eqn (1) for Ni(0), Cu(I) and Zn(II) complexes are plotted in Fig. 2. In the case of Ni complexes, the replacement of P by N in NiP_4 produces a positive heat of reaction (+5.57 kcal mol^{-1}). The heat of reaction is more positive for subsequent replacement, *i.e.* +6.28 and +10.93 kcal mol^{-1}. Clearly the Ni(0) system does not favor replacement of the soft ligand P by the hard ligand N. In fact, the complex NiN_4 is not observed as a stable species due to its unfavorable heat of formation. On the other hand, the replacement of soft ligands by the hard ligands in CuP_4 complex, produces negative (−8.11 kcal mol^{-1}) heat of reaction. The successive heat of formation values for the replacement of P by N in Cu(I) complexes are −7.45, −5.86 and −5.0 kcal mol^{-1}. The exothermic replacement of softer ligand P by hard ligand N in Cu(I) system suggests it is a hard ion, similar to Zn(II). However, the exothermicity decreases as the number of hard ligands in the coordination sphere of Cu(I) increases. The replacement of soft ligands P by hard ligand N in Zn(II) is an exothermic process that varies over a narrow range −16.17 to −16.78 kcal mol^{-1}.

$$\mathrm{M}P_xN_y + N \rightarrow \mathrm{M}P_{x-1}N_{y+1} + P \qquad (1)$$

Heat of reaction is ΔH_1, for $x = 4$, $y = 0$; ΔH_2 for $x = 3$, $y = 1$; ΔH_3 for $x = 2$, $y = 2$; ΔH_4 for $x = 1$, $y = 3$.

$$\mathrm{M}S_xW_y + W \rightarrow \mathrm{M}S_{x-1}W_{y+1} + S \qquad (2)$$

Heat of reaction is $\Delta H_1'$, for $x = 4$, $y = 0$; $\Delta H_2'$ for $x = 3$, $y = 1$; $\Delta H_3'$ for $x = 2$, $y = 2$; $\Delta H_4'$ for $x = 1$, $y = 3$.

Heats of reactions were also computed for the Cu(I) and Zn(II) complexes with a combination of H_2S (S) and H_2O (W) ligands. The values of $\Delta H'$, as defined in eqn (2) are plotted in Fig. 3. In the Cu(I) complexes, the replacement of S ligands by

Table 2 Selected bond distances (Å) and bond angles (°) of three- and four-coordinated Ni(0) complexes of PH_3 and NH_3

	System[a]						
	NiP_4	NiP_3N	NiP_2N_2	NiPN_3	NiP_3	NiP_2N	NiPN_2
Ni–P	2.256	2.237	2.194	2.220	2.213	2.200	2.136
Ni–N	—	2.124	2.148	2.116	—	2.025	2.069
P–Ni–P	109.47	109.53	107.59	—	120.00	115.93	—
P–Ni–N	—	109.40	112.42	127.11, 115.41	—	122.07	130.05
N–Ni–N	—	—	99.64	97.45, 98.94	—	—	104.42

[a] Ni = Ni(0), P = PH_3, N = NH_3.

Table 3 Selected bond distances (Å) and bond angles (°) of three- and four-coordinated Cu(I) complexes of H_2S and H_2O

	System[a]								
	CuS_4	CuS_3W	CuS_2W_2	CuSW_3	CuW_4	CuS_3	CuS_2W	CuSW_2	CuW_3
Cu–S	2.515	2.481	2.483	2.388	—	2.434	2.410	2.432	—
Cu–O	—	2.103	2.102	2.123	2.120	—	2.039	1.996, 2.043	2.189
S–Cu–S	112.25, 105.42, 103.09, 120.28, 110.71, 103.43	124.24, 115.31, 104.14	111.10	—	—	129.90, 114.42, 115.67	1.36	—	—
S–Cu–O	—	—	117.75, 121.38, 110.61, 96.14	111.53, 129.62, 126.65	—	—	110.52, 113.62	102.97, 133.44	—
O–Cu–O	—	110.27, 96.27	97.32	98.14, 86.28, 93.87	105.25, 108.42, 114.82	—	—	123.53	125.64, 105.58, 128.78

[a] Cu = Cu(I), S = H_2S, W = H_2O.

the W ligands produced a negative heat of reaction (exothermic) in a decreasing order. The heat of formation for CuS_3W from CuS_4 and W is −9.82 kcal mol^{-1} whereas the corresponding value for CuW_4 from CuW_3S and W is −7.33 kcal mol^{-1}. The sequential replacement of soft ligands (S) by hard ligands (W) produced more negative heats of reaction (exothermic) for Zn(II) complexes. The variation is within a small range of −20.11 to −20.39 kcal mol^{-1}.

The overall heat of formation for Ni(0), Cu(I) and Zn(II) complexes of N and P ligands with different combinations have been computed according to eqn (3) and the results are shown in Fig. 4. In the case of Ni(0), the heat of formation increases when the number of soft ligands increases in the coordination sphere. On the contrary, the heat of formation for Zn(II) complexes decreases as the number of soft ligands increases in the coordination sphere. Surprisingly, Cu(I) displays a heat of formation profile similar to Zn(II) although the heat of formation values for the former changes only marginally.

$$\mathrm{M} + (4 - n)P + nN \rightarrow [\mathrm{M}P_{4-n}N_n] \quad (3)$$

The overall heat of formation for Cu(I) and Zn(II) complexes of S and W ligands with different combinations have been calculated (eqn (4)) and the results are shown in Fig. 5. The overall heat of formation for the Zn(II) complex increases when the number of hard ligand increases in the coordination sphere. The heat of formation for Cu(I) also shows an increasing order when the number of hard ligand increases in the coordination sphere.

$$\mathrm{M} + (4 - n)S + \mathrm{n}W \rightarrow [\mathrm{M}S_{4-n}W_n] \quad (4)$$

3.3 Chemical hardness (η)

According to the principle of maximum hardness, when the hardness increases, the stability of the molecule also increases.[10] Chemical hardness is directly related to the stability of the molecule. An operational definition of chemical hardness (η) can be defined for a given chemical system using the following relationship (eqn (5)).[10]

$$\eta = (\mathrm{IP} - \mathrm{EA})/2 \quad (5)$$

Here η = chemical hardness (eV); IP = ionization potential; EA = electron affinity.

We have computed the chemical hardness for four-coordinated Cu(I) and Zn(II) complexes for different combinations of probe ligands (S, W, P and N). The chemical hardness profile for Ni(0), Cu(I) and Zn(II) complexes of P and N ligands with different combinations is shown in Fig. 6. In the case of Ni(0) complexes, the hardness increases as the number of soft ligands increases around the Ni(0) center. The hardness value gradually increases from +2.32 eV in NiN_3P to +3.27 eV in NiP_4. On the other hand the hardness (stability) decreases for Zn(II) complexes when the number of soft ligands increases in the coordination sphere. The hardness is highest in ZnN_4 (+13.41 eV) and lowest in ZnP_4 (+12.56 eV). In the case of Cu(I), the maximum hardness (7.34 eV) was computed for

Table 4 Selected bond distances (Å) and bond angles (°) of three- and four-coordinated Cu(I) complexes of PH_3 and NH_3

	System[a]								
	CuP_4	CuP_3N	CuP_2N_2	CuPN_3	CuN_4	CuP_3	CuP_2N	CuPN_2	CuN_3
Cu–P	2.457	2.470	2.467	2.447	—	2.409	2.404	2.408	—
Cu–N	—	2.117	2.136	2.156	2.171	—	2.058	2.069	2.082
P–Cu–P	109.47	107.76	107.62	—	—	119.99	116.18	—	—
P–Cu–N	—	111.12	109.70	109.45, 110.75	—	—	122.74, 121.08	117.63, 119.53	
N–Cu–N	—	—	110.35	109.18, 108.78	109.47	—	—	122.83	120.00

[a] Cu = Cu(I), P = PH_3, N = NH_3.

Table 5 Selected bond distances (Å) and bond angles (°) of three- and four-coordinated Zn(II) complexes of H_2S and H_2O

	System[a]								
	ZnS_4	ZnS_3W	ZnS_2W_2	ZnSW_3	ZnW_4	ZnS_3	ZnS_2W	ZnSW_2	ZnW_3
Zn–S	2.563	2.550	2.549	2.541	—	2.530	2.50	2.479	—
Zn–O	—	2.014	2.010	2.010	2.010	—	1.97	1.970	1.965
S–Zn–S	124.87, 101.30, 102.36, 108.49, 113.57, 104.00	114.38, 101.83, 126.77	120.79	—	—	135.49, 107.32, 117.09	142.89	—	—
S–Zn–O	—	110.87, 102.87, 98.724	116.90, 97.58	99.63, 113.84, 117.53	—	—	108.56	114.36	—
O–Zn–O	—	—	107.54	109.49, 108.10, 107.69	109.42, 107.69, 113.25	—	—	113.95	120.00

[a] Zn = Zn(II), S = H_2S, W = H_2O.

CuP_3N complex and this value is 0.16 eV larger than the hardness calculated for CuP_4 complex (7.18 eV). Not surprisingly, lowest hardness was calculated for CuN_4 that contains all hard donor ligands.

The trends in the computed hardness when ligands are H_2O (W) and H_2S (S) are shown in Fig. 7. In case of Zn(II) complexes, the chemical hardness decreases when the number of soft ligands around the Zn(II) center increases. The hardness difference between ZnW_4 and ZnS_4 is 1.12 eV. In contrast, the chemical hardness of CuS_4 is greater than that of CuW_4 by only 0.6 eV.

The chemical hardness has also been calculated for three-coordinated complexes of Ni(0), Cu(I) and Zn(II) with S, W, N and P ligands of different combinations. Metal complexes with P and N ligands are shown in Fig. 8 and with S and W ligands are shown in Fig. 9. The hardness of Ni(0) increases with the number of soft ligands in the coordination sphere. The trend is opposite for Zn(II) complexes. The highest hardness value was computed for NiP_3 and ZnN_3 among the three-coordinated Ni(0) and Zn(II) complexes considered here. The hardness of Cu(I) does not vary much when the number of soft ligands increases in the coordination sphere ranging from 7.55 to 8.20 eV. The highest value was computed for CuP_3.

3.4 Electronic chemical potential and electronegativity (χ)

The electronic chemical potential which is the negative of the electronegativity χ can be computed once IP and EA are available. These values have been calculated using eqn (6) for all three-coordinated species and the ligand discussed in Section 4.5.

$$\chi = (\mathrm{IP} + \mathrm{EA})/2 \qquad (6)$$

4 Discussion

4.1 Geometrical parameters of the optimized structures

The optimized structural parameters for Ni(0), Cu(I) and Zn(II) complexes of different hard and soft ligands with various combinations have been summarized in the Tables 1–6. The optimized structural parameters were compared for Cu(I) complexes with the synthetic complexes that are close to the model systems. The trend discovered in experimental system were reproduced reasonably well although Cu–L distances were almost always longer except in the case of Cu–OH_2 distance. The reason for this difference between calculated bond distances and experimentally observed distances could be due to the differences in the steric requirements of ligands characterized by X-ray crystallography, and due to the constraints present in experimental ligands which are typically chelating. The model systems pose no constraints as they are non-chelating in nature and bear only hydrogen.

4.2 Hardness based on calculated heat of formation

The heat of formation indicates the relative stability of the complexes along a series. The heat of formation of the typical

Table 6 Selected bond distances (Å) and bond angles (°) of three- and four-coordinated Zn(II) complexes of PH_3 and NH_3

	System[a]								
	ZnP_4	ZnP_3N	ZnP_2N_2	ZnPN_3	ZnN_4	ZnP_3	ZnP_2N	ZnPN_2	ZnN_3
Zn–P	2.595	2.604	2.613	2.627	—	2.541	2.540	2.536	—
Zn–N	—	2.111	2.116	2.122	2.130	—	2.074	2.074	2.072
P–Zn–P	109.47	108.72	107.98	—	—	120.00	120.24	—	—
P–Zn–N	—	110.25	109.46	108.35, 109.30	—	—	119.88	120.80	—
N–Zn–N	—	—	110.99	110.24	109.47	—	—	118.40	120.00

[a] Zn = Zn(II), P = PH_3, N = NH_3.

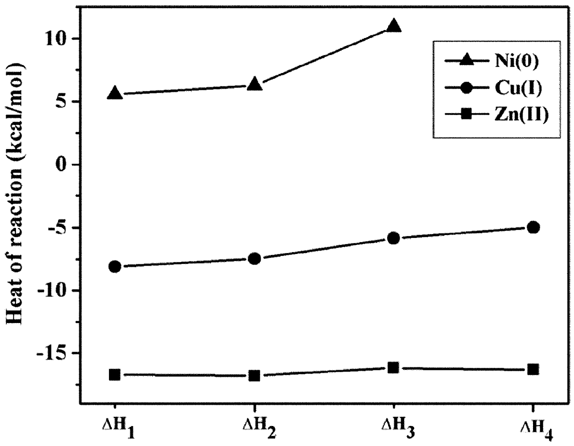

Fig. 2 Calculated heat of reaction for the substitution of soft ligand (P) by hard ligand (N) in the complex MP_xN_y where M = Ni(0), Cu(I), Zn(II), P = PH_3, N = NH_3. The generalized equation is $MP_xN_y + N \rightarrow MP_{x-1}N_{y+1} + P$ where x = 4–1, and y = 0–3. Heat of reaction is ΔH_1, when x = 4, y = 0; ΔH_2, x = 3, y = 1; ΔH_3, x = 2, y = 2; ΔH_4, x = 1, y = 3, respectively.

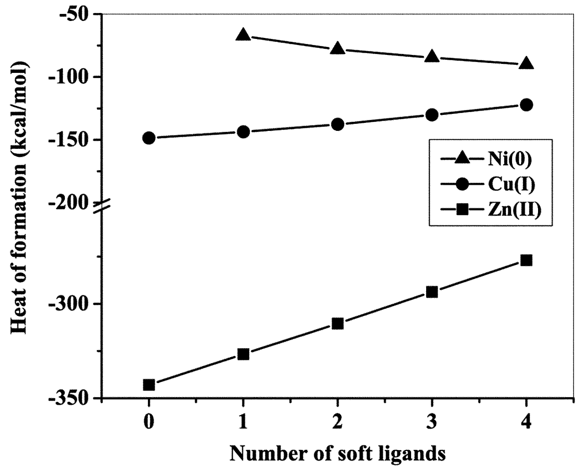

Fig. 4 Calculated heat of formation for the reaction M + N_{4-n} + $P_n \rightarrow [MN_{4-n}P_n]$ (n = 0–4) (M = Ni(0), Cu(I), Zn(II), P = PH_3, N = NH_3).

hard Zn(II) complexes of W, S, P and N ligands show the expected order. The Zn(II) system gains stabilization energy when hard ligands are added in the coordination sphere. The Ni(0) behaves as a typical soft center in contrast with the Zn(II) complexes. Replacement of soft ligands S and P from Ni(0) complexes by the hard ligands W and N leads to a less stable situation (endothermic). The hard ligands N and W do not form ML_4 type complexes with Ni(0) which is a further indication of its softness. The destabilization is significant when more than one W ligand replaces a S ligand from its coordination sphere and no stable complex results.

In the case of copper(I), the heat of formation profile is similar to the Zn(II) complexes. The replacement of S and P ligands by W and N ligands causes a gain in energy (exothermic) although the magnitude is less for copper(I) complexes when compared to Zn^{2+} analogs. This suggests that the Cu(I) center prefers hard ligands to be present in the coordination sphere similar to a hard center like Zn(II). This is an excellent agreement with some of the experimentally observed reactions for Cu(I). Recently Datta and co-workers have shown that the CuL_2ClO_4 reacts with water to give polymeric $[CuL(H_2O)(ClO_4)]_n$ complex in which the diphenylquinoxaline type ligand is replaced by the water molecule.[17] In these complexes (reactant and product), there is no soft ligand around the copper(I) ion. There are other examples in which the Cu(I) is surrounded by one hard ligand and three soft ligands.[18,19] Pilloni *et al.* demonstrated that the Cu(I) forms only CuP_2O_2 (Cu = Cu(I), P = phosphine functionalized ferrocene, O = phosphine oxide functionalized ferrocene) complex when the reaction was carried out for Cu(I) with phosphine oxide functionalized ferrocene and phosphine functionalized ferrocene.[20] This reaction does not yield the CuP_4

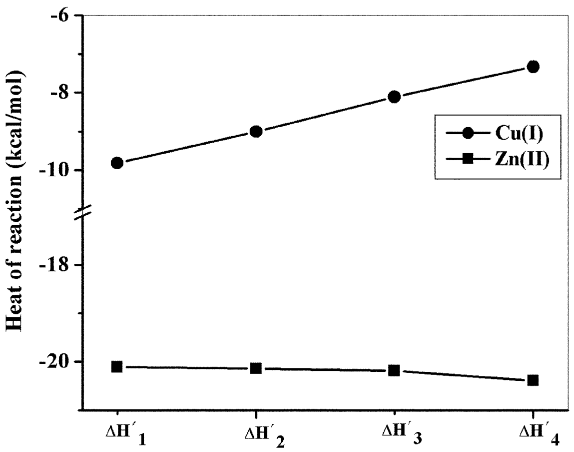

Fig. 3 Calculated heat of reaction for the substitution of soft ligand (S) by hard ligand (W) in the complex MS_xW_y where M = Cu(I), Zn(II), S = H_2S, W = H_2O. The generalized equation is $MS_xW_y + W \rightarrow MS_{x-1}W_{y+1} + S$ where x = 4–1, and y = 0–3. Heat of reaction is $\Delta H_1'$, when x = 4, y = 0; $\Delta H_2'$, x = 3, y = 1; $\Delta H_3'$, x = 2, y = 2; $\Delta H_4'$, x = 1, y = 3, respectively.

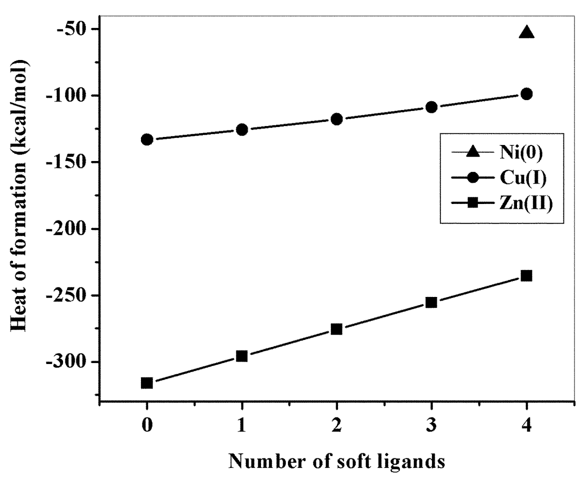

Fig. 5 Calculated heat of formation for the reaction M + (4 − n) S + $n\,W \rightarrow [MS_{4-n}W_n]$ (n = 0–4) (M = Ni(0), Cu(I), Zn(II), W = H_2O, S = H_2S).

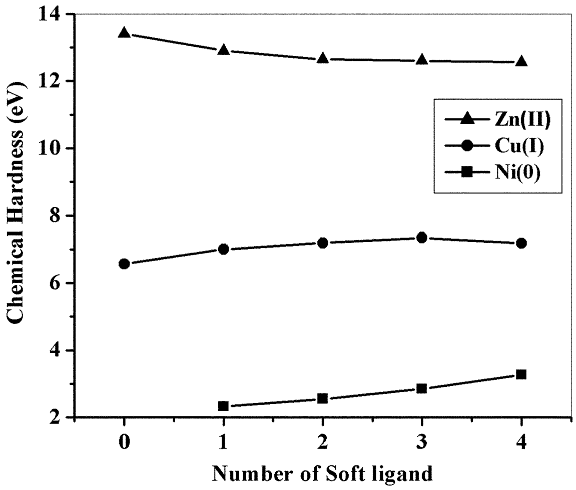

Fig. 6 Calculated chemical hardness (η) for the [M$N_{4-n}P_n$] (n = 0–4) complex (M = Ni(0), Cu(I), Zn(II), P = PH_3, N = NH_3 using vertical IP and EA.

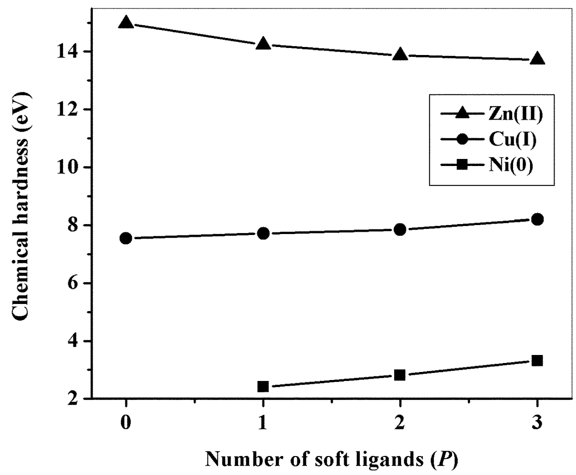

Fig. 8 Calculated chemical hardness (η) for the [M$N_{3-n}P_n$] (n = 0–3) complex (M = Ni(0), Cu(I), Zn(II), P = PH_3, N = NH_3) using vertical IP and EA.

complex, which has been predicted based on the HSAB principle assuming copper(I) to be a soft ion. There are several other situations where the HSAB principle has failed to explain the ligand composition of Cu(I) complexes and their reactivities.[7] It has been recently pointed out that differences in chemical potential, entropy, polarization and electrostatic effects can make a difference in the analysis of the HSAB principle.[21] In the case of ligand preferences of Cu(I), the electronic chemical potential and electrostatic effects are making it similar to Zn(II) rather than Ni(0).

4.3 Hardness based on vertical IP and EA

The chemical hardness can be directly estimated using the vertical ionization potentials and the electron affinities in their ground state geometries. They were calculated for four-coordinated as well as for three-coordinated complexes of Ni(0), Cu(I) and Zn(II) and are graphically shown with various combinations of S, W, P and N ligands in Fig. 6 and 7. In the case of P and N complexes of Cu(I), the maximum hardness was calculated for the CuP_3N complex and not for CuP_4 complex. The greater stability for CuP_3N complexes suggests that copper would like a combination of hard and soft ligands in its coordination sphere indicating the ambivalent nature of Cu(I). It is interesting to note that experimental observations also point to maximum stability for systems with three soft and one hard ligand rather than four soft ligands. The most stable Ni(0) and Zn(II) complexes are ZnN_4 and NiP_4 based on the hardness values as expected for a typical soft metal and hard metal like Ni(0) and Zn(II), respectively.

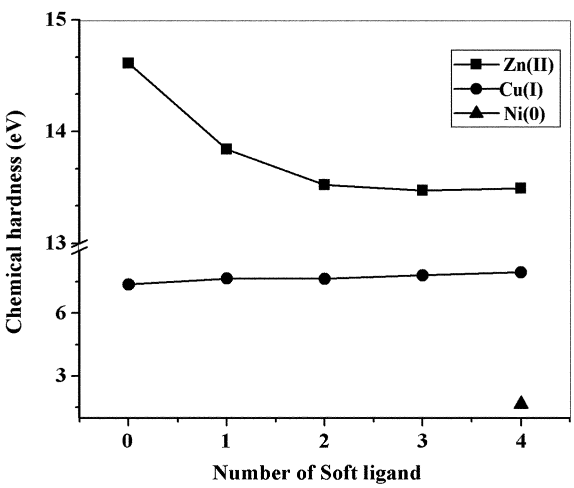

Fig. 7 Calculated chemical hardness (η) for the [M$W_{4-n}S_n$] (n = 0–4) complex (M = Ni(0), Cu(I), Zn(II), S = H_2S, W = H_2O) using vertical IP and EA.

In the case of H_2S and H_2O complexes of Zn(II), the hardness (stability) increases as the number of hard ligands increases in the coordination sphere (Fig. 7). This is expected for the typical hard center like Zn(II). In the case of copper(I) complexes of S and W, slightly more hardness (stability) was calculated for CuS_4. For Ni(0) complexes, the hardness goes down when the number of hard ligands increases in the coordination sphere. Ni(0) prefers only soft ligands in its coordination sphere.

The hardness (stability) of three-coordinated complexes of Ni(0) also increases with increasing the number of soft ligands P and S in the coordination sphere (Fig. 8 and 9). On the other hand the hardness (stability) of Zn(II) complexes increases with increasing the number of hard ligands in the coordination sphere. The most stable three-coordinated Cu(I) complex however, is CuP_3 as computed from the hardness data. The chemical hardness values of the three-coordinated Cu(I) complexes vary marginally with the nature of the ligands involved.

4.4 Maximization of hardness

The generality of the principle of maximum hardness[12] has been challenged on the basis of theoretical grounds[22] and so it would be appropriate to verify its applicability in the current system. Although, Cu(I) behaves like Zn(II) in its preference for hard ligands, one can find out if the absolute hardness is higher or lower on addition of a hard ligand. The stabilization of hard metal ion, Zn(II), is achieved with the addition of hard

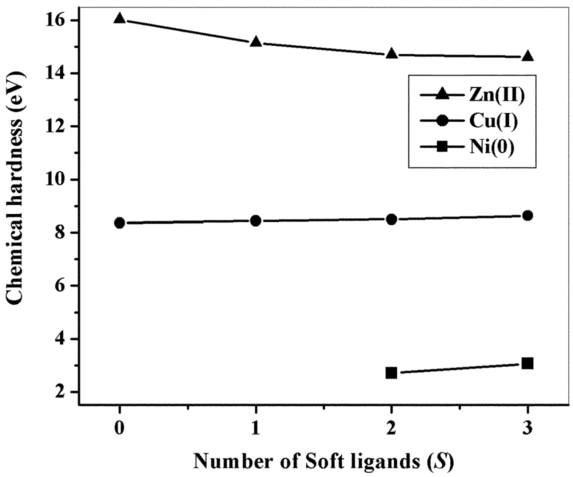

Fig. 9 Calculated chemical hardness (η) for the [$MW_{3-n}S_n$] (n = 0–3) complex (M = Ni(0), Cu(I), Zn(II), S = H_2S, W = H_2O) using vertical IP and EA.

ligands W and N rather than S and P. This leads to the maximization of the hardness (Fig. 6 and 7). For soft metal Ni(0) the stabilization has been achieved with the addition of soft ligands S and P rather than W and N (Fig. 6). This also leads to the maximization of the hardness. In the case of Cu(I) the maximum hardness was achieved for $CuNP_3$ complex (Fig. 6). When the ligands are W and S, the maximum hardness of Cu(I) was computed for CuS_4 as expected for a traditional soft cation (Fig. 7). Maximization of hardness appears to have occurred in the complexes predicted to be most stable on the basis of experimental data.

4.5 Is copper an exception to the HSAB principle?

The heats of reactions for Cu(I) complexes in this study follow the trend observed by Zn(II) complexes rather than those of Ni(0), a typical soft acid. It is clear that copper(I) does not follow the HSAB principle. Another recent study has also pointed out a similar anomaly in the preference of (soft) Ag^+ and (hard) H^+ for a variety of ligands.[23] We made an attempt to examine orbital interactions in the mixed ligand complexes

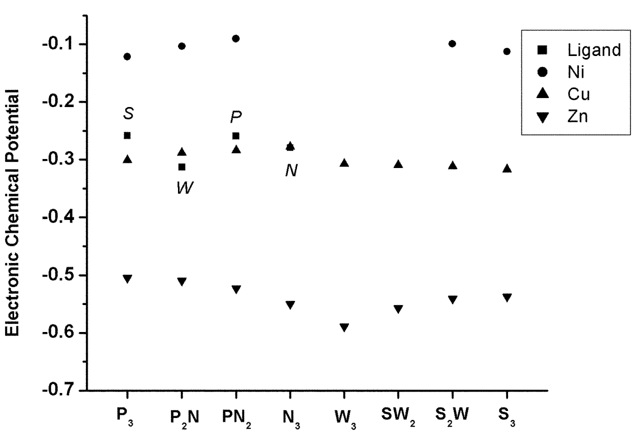

Fig. 10 Calculated electronic chemical potential (μ) for ML_3 complexes (M = Ni(0), Cu(I), Zn(II)), P = PH_3, N = NH_3, S = H_2S, W = H_2O) using vertical IP and EA.

to gain a better understanding of the binding preferences. We could not find a significant "orbital" or "electronic" effect. Quantification of metal–ligand bonding probed through density functional theory may provide an answer to these puzzles, but is quite involved.[24] As pointed out by Ayers,[21] the electronic chemical potential ($-\chi$) has to be the same for the HSAB principle to be valid. The electronic chemical potential of L and ML_3 species examined in this study are readily obtained from the computed IP and EA values. For electron density to flow from the ligand to the metal, the global electronic chemical potential of the metal should be lower than that of the ligand. In $[ZnL_3]^{2+}$ this condition is satisfied. However, in the case of $[CuL_3]^+$ this condition is not satisfied in all cases (Fig. 10). Hence, the application of HSAB to Cu(I) and Ni(0) is unlikely to yield correct results under these circumstances.

5 Conclusion

In the absence of steric constraints, one expects all complexes of d^{10} metal ions to form tetrahedral complexes. Consistent with this expectation, all complexes optimized close to the ideal tetrahedral geometry. The bond distances were as expected for Cu(I)–S/P and Cu(I)–W/N complexes. The geometry of mixed ligand complexes with various ratios of S/W and P/N are comparable to the changes observed in structurally characterized complexes. In spite of this general agreement with experiment, the computed heat of formation data do not support the unequivocal classification of Cu(I) ion as a soft metal ion.

Although heats of formation are not in accord with HSAB predictions, the absolute hardness from the computed IP and EA is in accord with the stability of complexes observed experimentally. Copper(I) would prefer to have a balance in the number of hard or soft ligands around it. The number of hard ligands tolerated by a soft acceptor like Ni(0) is also limited and dependent on the ligand. The difficulty in applying HSAB theory in these systems is resolved by examining the electronic chemical potential. The electronic chemical potential of the metal and precursor complexes should be lower than the electronic chemical potential of the ligands for HSAB theory to be applicable. The calculated values of χ are very similar for copper(I) and the ligands. Under these conditions, the HSAB predictions are unlikely to be followed.

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