Stability of Transition Metal Complexes Halides of the Nickel Metal

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ABSTRACT

The stability of coordination complex is an important factor that decides the stability and reactivity of a metal complex. The stability of metal complex is governed by two different aspects such as thermodynamic and kinetic stabilities. The stability of metal complex generally means that it exists under favorable conditions without undergoing decomposition and has a considerable shelf life period. The term stability of metal complex cannot be generalized since the complex may be stable to one reagent/condition and may decompose in presence of another reagent/condition. The stability of metal complexes can be explained with the help of two different aspects, namely, thermodynamic stability and kinetic stability. Nevertheless, a metal complex is said to be stable if it does not react with water, which would lead to a decrease in the free energy of the system, i.e., thermodynamic stability. On the other hand, the complex is said to possess kinetic stability if it reacts with water to form a stable product and there is a known mechanism through which the reaction can proceed. For example, the system may not have sufficient energy available to break a strong bond, although once the existing bond is broken it could be replaced by new bond which is stronger than the older one. Stability of complex compound is assigned to be its

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existence in aqueous solution with respect to its bond dissociation energy, Gibbs free energy, standard electrode potential, pH of the solution, and rate constant or activation energy for substitution reactions.

The crystal field stabilization energy (CFSE) is an important factor in the stability of transition metal complexes. Complexes with high CFSE tend to be thermodynamically stable (i.e., they have high values of K_a , the equilibrium constant for metal-ligand association) and are also kinetically inert. They are kinetically inert because ligand substitution requires that they dissociate (lose a ligand), associate (gain a ligand), or interchange (gain and lose ligands at the same time) in the transition state. These distortions in coordination geometry lead to a large activation energy if the CFSE is large, even if the product of the ligand exchange reaction is also a stable complex. For this reason, complexes of Pt^{4+} , Ir^{3+} (both low spin 5d⁶), and Pt^{2+} (square planar 5d⁸) have very slow ligand exchange rates.

There are two other important factors that contribute to complex stability:

Hard-soft interactions of metals and ligands (which relate to the energy of complex formation)

The chelate effect, which is an entropic contributor to complex stability.

KEYWORDS: transition metal, complexes, halides, stability, nickel, coordination, ligand, thermodynamic

INTRODUCTION

Hard acids are typically small, high charge density cations that are weakly polarizable such as H^+ , Li^+ , Na⁺, Be²⁺, Mg²⁺, Al³⁺, Ti⁴⁺, and Cr⁶⁺. Electropositive metals in high oxidation states are typically hard acids. These elements are predominantly found in oxide minerals, because O²⁻ is a hard base.[1,2] Some hard bases include H₂O, OH⁻, O²⁻, F⁻, NO₃⁻, Cl⁻, and NH₃.

The hard acid-base interaction is primarily electrostatic. Complexes of hard acids with hard bases are stable because of the electrostatic component of the CFSE.

Soft acids are large, polarizable, electronegative metal ions in low oxidation states such as Ni^0 , Hg^{2+} , Cd^{2+} , Cu^+ , Ag^+ , and Au^+ .

Soft bases are anions/neutral bases such as H^- , C_2H_4 , CO, PR₃, R₂S, and CN⁻). Soft acids typically occur in nature as sulfide or arsenide minerals.

The bonding between soft acids and soft bases is predominantly covalent. For example, metal carbonyls bind through a covalent interaction between a zero- or low-valent metal and neutral CO to form $Ni(CO)_4$, $Fe(CO)_5$, $Co(CO)_4^-$, $Mn_2(CO)_{10}$, $W(CO)_6$, and related compounds.

Hydrodehalogenation is an effective strategy for transforming persistent and potentially toxic organohalides into their more benign congeners. Common methods utilize Pd/C or Raney-nickel as catalysts, which are either expensive or have safety concerns. A nickel-based catalyst supported on titania (Ni-phen@TiO₂-800) is used as a safe alternative to pyrophoric Raney-nickel. The catalyst is prepared in a straightforward fashion by deposition of nickel (II)/1,10-phenanthroline on titania, followed by pyrolysis. The catalytic material, which was characterized by SEM, TEM, XRD, and XPS,

consists of nickel nanoparticles covered with N-doped carbon layers. By using design of experiments (DoE), this nanostructured catalyst is found to be proficient for the facile and selective hydrodehalogenation of a diverse range of substrates bearing C–I, C–Br, or C–Cl bonds (>30 examples). The practicality of this catalyst system is demonstrated by the dehalogenation of environmentally hazardous and polyhalogenated substrates atrazine, tetrabromobisphenol A, tetrachlorobenzene, and a polybrominated diphenyl ether (PBDE).

Hydrodehalogenation of 35 different aryl halides (Ar–I, Ar–Br, and Ar–Cl) is performed using a heterogeneous nickel catalyst (Ni-phen@TiO₂-800) and molecular hydrogen. This work represents an effective strategy for converting thermally and chemically inert hazardous compounds into their less noxious congeners. Characterization of the catalyst reveals nickel nanoparticles covered with N-doped carbon layers.[3,4]



Hydrodehalogenation is an effective strategy for transforming persistent and potentially toxic organohalides into their more benign congeners. Common methods utilise Pd/C or Raney-nickel as catalysts, which are either expensive or have safety concerns. Herein, we report a nickel-based catalyst supported on titania (Ni-phen@TiO 2 -800) as a safe alternative to pyrophoric Raney-nickel. The catalyst is prepared in a straightforward fashion via deposition of nickel (II)/1,10-phenanthroline on titania, followed by pyrolysis. The catalytic material-which was characterised by SEM, TEM, XRD, and XPS-consists of nickel nanoparticles covered with N-doped carbon layers. Using experimental design (DoE), this nano-structured catalyst is proficient for the facile and selective hydrodehalogenation of a diverse range of substrates bearing C-I, C-Br, and C-Cl bonds (>30 examples). The practicality of this catalyst system is demonstrated by the dehalogenation of environmentally hazardous and polyhalogenated substrates atrazine, tetrabromobisphenol A, tertrachlorobenzene and a polybrominated diphenyl ether (PBDE).[5,6]





XPS survey spectrum of Ni-Phen@TiO 2 -800 catalyst (a) and high-resolution deconvoluted XPS spectra for Ni 2p (b), C 1s (c), O 1s (d), N 1s (e) and Ti 2p (f).

Discussion

Substitution of phosphine ligands in nickel(II) halide complexes by now attractive N-heterocyclic carbene (NHC) ligands is one of the well-known organometallic reactions. New, simple, and easy-to-prepare nickel(II) halides bearing both a phosphine and an NHC ligand, [NiX2(PPh3)(NHC)], were synthesized by the reaction of [NiX2(PPh3)2] (X = Cl and Br) with 1 equiv of a bulky NHC ligand. Rather small NHC ligands did not form NHC/PR3 mixed complexes. Controlling the amount of the NHC ligand and purification led to successful isolation in good to moderate yields and structural determination of these carbene complexes. Studies on catalytic Grignard cross-coupling reactions using three complexes, the NHC/PPh3 mixed complex, a "bis"-carbene complex, and [NiCl2(PPh3)2], revealed that the monocarbene complex catalyzes reactions with the highest activity, but, in comparison, catalysis does not proceed well using the latter two complexes.[7,8]





A dependence of the formation of tri-n-octylphosphine-capped Ni nanocrystals on the presence of halide ions during their synthesis is shown. For the application-oriented synthesis of Ni particles, this information can be crucial. Furthermore, Ni nanoparticles can be converted to nickel phosphide or sulphide by heating them up in the presence of a phosphorus or sulphur source, resulting in either solid or hollow nanocrystals, formed via the nanoscale Kirkendall effect, depending on the synthesis route. By adjusting the Ni crystallite size in the initial nanoparticles via the halide ion concentration the cavity size of the resulting hollow nanocrystals can be tuned, which is otherwise impossible to realise for particles of a similar total diameter by using this process. The synthesised hollow Ni₃S₂ nanocrystals exhibit a much sharper localised surface plasmon resonance (LSPR) band than all previously presented particles of this material, which is known to show molar extinction coefficients at the LSPR maximum similar to Au. This narrow linewidth could be explained by the nanoparticles' high crystallinity resulting from the Kirkendall process and is interesting for various possible optical applications such as surface-enhanced Raman spectroscopy owing to the low cost of the involved materials compared to the widely used noble metals.[9,10]

The syntheses of three series of complexes designed with self-complementary motifs for formation of halogen bonds between an iodotetrafluorophenyl ligand and a halide ligand at square-planar nickel are reported, allowing structural comparisons of halogen bonding between all four halides $C_6F_4I\cdots X-Ni$ (X = F, Cl, Br, I). In the series trans-[NiX(2,3,5,6-C_6F_4I)(PEt_3)_2] 1pX and trans-[NiX(2,3,4,5-C_6F_4I)(PEt_3)_2] (X = F, Cl, Br, I) 1oX, the iodine substituent on the benzene ring was positioned para and ortho to the metal, respectively. The phosphine substituents were varied in the series, trans-[NiX(2,3,5,6-C_6F_4I)(PEt_2Ph)_2] (X = F, I) 2pX. Crystal structures were obtained for the complete series 1pX, and for 1oF, 1oCl, 1oI and 2pI. All these complexes exhibited halogen bonds in the solid state, of which 1pF exhibited unique characteristics with a linear chain, the shortest halogen bond d(C₆F_4I···F–Ni) = 2.655(5) Å and the greatest reduction in halogen bond distance (I···F) compared to the sum of the Bondi van der Waals radii, 23%. The remaining complexes form zig-zag chains of halogen bonds with distances also reduced with respect to the sum of the van der Waals radii. The magnitude of the reductions follow the pattern F > Cl ~ Br > I, 1pX > 1oX, consistent with the halogen bond strength following

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the same order. The variation in the I···X–Ni angles is consistent with the anisotropic charge distribution of the halide ligand. The temperature dependence of the X-ray structure of 1pF revealed a reduction in halogen bond distance of 0.055(7) Å on cooling from 240 to 111 K. Comparison of three polymorphs of 1oI shows that the halogen bond geometry may be altered significantly by the crystalline environment. The effect of the halogen bond on the ¹⁹F NMR chemical shift in the solid state is demonstrated by comparison of the magic-angle spinning NMR spectra of 1pF and 1oF with that of a complex incapable of halogen bond formation, trans-[NiF(C₆F₅)(PEt₃)₂] 3F. Halogen bonding causes deshielding of δ_{iso} in the component of the tensor perpendicular to the nickel coordination plane. The results demonstrate the potential of fluoride ligands for formation of halogen bonds in supramolecular structures.[11,12]



A. Formation of halogen bonds with nickel fluoride in solution and (b) structural motif with envisaged intermolecular halogen-bonding interaction.





Dinuclear product [trans-NiX(PEt₃)₂]₂(µ-2,3,5,6-C₆F₄).

Results

In another work, fabricated solar cells with the hybrid metal halide compounds with the general formula ABX₃, where cation the А is methylammonium, the B cation is nickel, and the X anion is chlorine or a mixture of chlorine and iodine. We obtained experimental evidence that this material is a semiconductor with an orthorhombic crystalline structure which pertains to the space group Cmcm. The bandgap can be modulated from 1.4 eV to 1.0 eV by changing the chlorine anion to iodine. Therefore, we were able to obtain solar cells with efficiencies up to 0.16% with the CH₃NH₃NiCl₂I composition. We have also studied by means of first-principles calculations, taking into account van der Waals dispersive forces, the ground state properties of these materials such as their crystal structure and formation and decomposition energies. We have found that these energies are lowered by the lighter mass anion, and the calculated decomposition energies show that only CH₃NH₃NiCl₃ is stable with respect to the most probable decomposition pathway. The electronic band structure and band edge alignments have been

calculated using quasiparticle effects through the GW_0 approximation; these materials show an indirect bandgap with the valence band maxima at -6.93 and -5.49 eV with respect to vacuum and the conduction band minima at -5.62 and -4.60 eV with respect to vacuum for CH₃NH₃NiCl₃ and CH₃NH₃NiI₃, respectively.[13,14]

Magnetic measurements on variously hydrated nickel chlorides and bromides, including deuterated forms, are reported. Results include locations and sizes of susceptibility maxima, T_{max} and χ_{max} , ordering temperatures T_c , Curie constants and Weiss theta in the paramagnetic regime, and primary and secondary exchange interactions from analysis of low temperature data. For the latter a 2D Heisenberg model augmented by interlayer exchange in a mean-field approximation is applied. Magnetization data to 16 kG as a function of temperature show curvature and hysteresis characteristics quite system dependent. For four materials high field magnetization data to 70 kG at 2.00 K are also obtained. Comparison is made with theoretical relations for spin-1 models. Trends

are apparent, primarily that T_{max} of each bromide hydrate is less than for the corresponding chloride, and that for a given halide nD₂O (n=1 or 2) deuterates exhibit lesser T_{max} than do nH₂O hydrates. A monoclinic unit cell determined from powder X-ray diffraction data on NiBr₂· 2D₂O is different from and slightly larger than that of NiBr₂· 2H₂O.

Hydrated 3d transition metal chlorides are a very important class of insulating magnets. Many examples, in particular among the common hydration forms di-, tetra- and hexahydrate, have served as notable examples of definite magnetic model systems, e.g., three-dimensional Heisenberg antiferromagnet [1], [2]. So it is somewhat surprising that corresponding bromide materials are much less thoroughly studied. Potentially fruitful comparisons of, for example, exchange interactions via metal ion-(di)halide-metal ion pathways could emerge.

In order to further such examination we report here susceptibility and magnetization data on NiBr2·2H2O and NiBr2·H2O. NiCl2·2H2O is characterized by linear chains of chloride bibridged metal ions, with slightly less than 90° Cl-Ni-Cl bridging angles. Slight relative tilting of adjacent NiCl₄ planar coordination units along the chain leads to a repeat unit of two nickel centers. Crystallization is in a monoclinic C2/m structure, with NiCl₂NiCl₂NiCl₂Ni... chains along the b axis. Chains are coupled structurally by hydrogen bonding. The unit-cell volume per formula unit is 105.0 Å^3 . NiCl₂· 2H₂O is a nearly isotropic 3D Heisenberg antiferromagnet ordering at 7.25 K, with a spin reorientation transition at 6.31 K .The spins in each NiCl₂NiCl₂Ni... chain are ferromagnetically aligned along a*, normal to both b and c. Spins of chains separated by $\pm (a \pm c)/2$ are oppositely directed to give overall antiferromagnetism. A metamagnetic transition occurs at 19 kG near 0 K, followed by transitions at 56 and 82 kG, to states of increasing ferromagnetic alignment. Spins are very nearly along metal-oxygen bonds, which are essentially normal to the $MCl_2MCl_2M...$ Strong chains. ferromagnetic intrachain and somewhat weaker but still significant antiferromagnetic interchain exchange interactions exist.

The only other NiX₂·nH₂O (n=1 or 2) structure determined, only partially, is that of NiBr₂·2H₂O. The unit cell is isomorphic with that of the chloride, in monoclinic space group I2/m with Z=4. Lattice parameters are from 3.8% to 5.0% larger in the bromide; these are a=7.21(1) and 6.9093(5) Å, b=7.23(1) and 6.8858(6) Å, and c=9.17(1) and 8.8298(4) Å for NiBr₂·2H₂O and NiCl₂·2H₂O respectively, with β =92.4(3)° and 92.246(2)° in the same order. Heat capacity data indicate successive magnetic transitions occurring at 6.23 and 5.79 K, presumably analogous to those in the chloride but at somewhat lower temperatures .[15,16]

Another point of major interest arises. The effects of deuteration on the magnetic properties of transition metal compounds containing hydrogen, including those with waters of hydration, are typically quite small, though the literature is not extensive. This need not necessarily be the case however, since such effects are a function of structural details, especially if coordinated waters provide important super exchange pathways. Our report on $MnCl_2 \cdot D_2O$ and $CoCl_2 \cdot D_2O$ is a significant recent example. Therefore we also prepare and examine each D_2O containing nickel chloride and nickel bromide hydration form. Significant contrasts with the H₂O containing materials appear, somewhat more pronounced for bromides than for chlorides.[17,18]

Conclusions

An estimated 2.7 million tonnes (t) of nickel per year are mined worldwide; Indonesia (1,000,000 t), the Philippines (370,000 t), Russia (250,000 t), New Caledonia (190,000 t), Australia (160,000 t) and Canada (130,000 t) are the largest producers as of 2021. The largest nickel deposits in non-Russian Europe are in Finland and Greece. Identified landbased sources averaging at least 1% nickel contain at least 130 million tonnes of nickel. About 60% is in laterites and 40% is in sulfide deposits. Also, extensive nickel sources are found in the depths of the Pacific Ocean, especially in an area called the Clarion Clipperton Zone in the form of polymetallic nodules peppering the seafloor at 3.5–6 km below sea level. These nodules are composed of numerous rare-earth and are estimated to be 1.7% metals nickel.[19,20]With advances in science and engineering, regulation is currently being set in place by the International Seabed Authority to ensure that these nodules are collected in an environmentally conscientious manner while adhering to the United Nations Sustainable Development Goals. The one place in the United States where nickel has been profitably mined is Riddle, Oregon, with several square miles of nickel-bearing garnierite surface deposits. The mine closed in 1987. The Eagle mine project is a new nickel mine in Michigan's Upper Peninsula. Construction was completed in 2013, and operations began in the third quarter of 2014. In the first full year of operation, the Eagle Mine produced 18,000 t.[21]

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References

- [1] "Standard Atomic Weights: Nickel". CIAAW. 2007.
- Pfirrmann, Stefan; Limberg, Christian; Herwig, Christian; Stößer, Reinhard; Ziemer, Burkhard (2009). "A Dinuclear Nickel(I) Dinitrogen Complex and its Reduction in Single-Electron Steps". Angewandte Chemie International Edition. 48 (18): 3357–61. doi: 10.1002/anie.200805862. PMID 19322853.
- [3] Carnes, Matthew; Buccella, Daniela; Chen, Judy Y. -C.; Ramirez, Arthur P.; Turro, Nicholas J.; Nuckolls, Colin; Steigerwald, Michael (2009). "A Stable Tetraalkyl Complex of Nickel (IV)". Angewandte Chemie International Edition. 48 (2): 290–4. doi: 10. 1002/anie. 200804435. PMID 19021174.
- [4] Anthony, John W.; Bideaux, Richard A.; Bladh, Kenneth W.; Nichols, Monte C., eds. (1990).
 "Nickel" (PDF). Handbook of Mineralogy. Vol. I. Chantilly, VA, US: Mineralogical Society of America. ISBN 978-0962209703.
- [5] "Nickel: Nickel mineral information and data". SRD Mindat.org. Archived from the original on March 3, 2016. Retrieved March 2, 2016. national Journal J
- [6] Stixrude, Lars; Waserman, Evgeny; Cohen, Ronald (November 1997). "Composition and temperature of Earth's inner core". Journal of [16] Geophysical Research. 102 (B11): 24729– 24740. Bibcode: 1997JGR... 10224729S. doi: 10.1029/97JB02125.
- [7] Coey, J. M. D.; Skumryev, V.; Gallagher, K. (1999). "Rare-earth metals: Is gadolinium really ferromagnetic?". Nature. 401 (6748): 35–36. Bibcode: 1999Natur. 401... 35C. doi:10.1038/43363. S2CID 4383791.
- [8] "Nickel Use In Society". Nickel Institute. Archived from the original on September 21, 2017.
- [9] Treadgold, Tim. "Gold Is Hot But Nickel Is Hotter As Demand Grows For Batteries In Electric Vehicles". Forbes. Retrieved October 14, 2020.
- [10] "Nickel Compounds The Inside Story". Nickel Institute. Archived from the original on August 31, 2018.

- [11] Mulrooney, Scott B.; Hausinger, Robert P. (June 1, 2003). "Nickel uptake and utilization by microorganisms". FEMS Microbiology Reviews. 27 (2-3): 239–261. doi:10.1016/S0168-6445(03)00042-1. ISSN 0168-6445. PMID 12829270.
- [12] Shiozawa, Hidetsugu; Briones-Leon, Antonio; Domanov, Oleg; Zechner, Georg; et al. (2015). "Nickel clusters embedded in carbon nanotubes as high performance magnets". Scientific Reports. 5: 15033. Bibcode: 2015NatSR... 515033S. doi:10.1038/srep15033. PMC 4602218. PMID 26459370.
- [13] Kittel, Charles (1996). Introduction to Solid State Physics. Wiley. p. 449. ISBN 978-0-471-14286-7.
- [14] Hammond, C. R.; Lide, C. R. (2018). "The elements". In Rumble, John R. (ed.). CRC Handbook of Chemistry and Physics (99th ed.).
 Boca Raton, FL: CRC Press. p. 4. 22. ISBN 9781138561632.
- [15] ^ Sharma, A.; Hickman, J.; Gazit, N.; Rabkin, E.; Mishin, Y. (2018). "Nickel nanoparticles set a new record of strength". Nature Communications. 9 (1): 4102. Bibcode: Scien 2018NatCo... 9. 4102S. doi:10.1038/s41467-ch an 018-06575-6. PMC 6173750. PMID 30291239.
 - 5] Scerri, Eric R. (2007). The periodic table: its story and its significance. Oxford University Press. pp. 239–240. ISBN 978-0-19-530573-9.
- [17] Miessler, G. L. and Tarr, D. A. (1999) Inorganic Chemistry 2nd ed., Prentice–Hall. p. 38. ISBN 0138418918.
- [18] Petrucci, R. H. et al. (2002) General Chemistry 8th ed., Prentice–Hall. p. 950. ISBN 0130143294.
- [19] NIST Atomic Spectrum Database Archived March 20, 2011, at the Way back Machine To read the nickel atom levels, type "Ni I" in the Spectrum box and click on Retrieve data.
- [20] Kondev, F. G.; Wang, M.; Huang, W. J.; Naimi, S.; Audi, G. (2021). "The NUBASE2020 evaluation of nuclear properties" (PDF). Chinese Physics C. 45 (3): 030001. doi: 10.1088/1674-1137/abddae.
- [21] "Isotopes_of_nickel". www.chemeurope.com. Retrieved September 2, 2022.