

Production of Thiosulfate Anion from the Reaction of Bis(dialkyldithiocarbamato)nickel(II) Complexes with Ethylenediamine

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Synopsis. Planar divalent nickel dithiocarbamates Ni(dtc)₂ (dtc[−] = dithiocarbamate anions) show interesting reactivity patterns in their reactions with Lewis bases. These complexes form mixed ligand complexes with PR₃ easily. But, simple hard nitrogen bases do not displace all the nickel dithiocarbamates. A chelating base like en displaces the dithiocarbamate anion completely from the complexes and formed pink colored solution in an aqueous medium. The chromophore was identified to be [Ni(en)₃]²⁺ and the counter anion was dtc[−]. On ageing, pink crystals separated out from the solution. Chemical analysis of the crystals showed a 1:2 ratio of Ni to S and the absence of dtc[−] ion. The possibility of S₂O₃^{2−} being the counter anion was tested. Even though infrared spectrum could not confirm the S₂O₃^{2−} anion, the final confirmation came from the X-ray analysis of the authentic crystals. This is a rare occasion of metal ion catalyzed oxidation of S^{2−} to S₂O₃^{2−} ions.

The interaction of transition metal dithiocarbamates with Lewis bases leads to the formation of the corresponding base adducts.^{1–3} Bis(dialkyldithiocarbamato)nickel(II) complexes, [Ni(dtc)₂] show interesting variations in their reactions with Lewis bases.⁴ Bis(diethyldithiocarbamato)nickel(II) was shown to form an adduct with pyridine only at liquid nitrogen temperature whereas similar complexes with electron-withdrawing substituents on the dithiocarbamate moiety formed adduct with ease at ambient temperature.⁵ Other than the adduct formation reaction, similar complexes were also shown to promote redox reactions of the ligands under the basic conditions. A copperthiol complex [Cu(RSH)₂Cl] in pyridine was shown to oxidize thioamides, thiols, sulfide ion and sulfur to sulfate ion.⁶ Here, we report the first instance of a dithiocarbamate moiety getting oxidized to S₂O₃^{2−} in a basic solution. The following dithiocarbamates, (I) bis(diethyldithiocarbamato)nickel(II), [(C₂H₅)₂NCS₂]₂Ni; (II) bis[(2-hydroxyethyl)dithiocarbamato]nickel(II), [(HOC₂H₄)HNCS₂]₂Ni, and (III) bis[bis(2-hydroxyethyl)dithiocarbamato]nickel(II), [(HOC₂H₄)₂NCS₂]₂Ni; were allowed to interact with the Lewis bases and the interesting redox reactions associated with them are reported here.

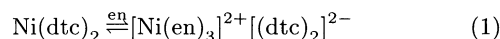
Results and Discussion

Interaction with Pyridine: The three dithiocarbamates [Ni(dtc)₂], I, II, and III, when treated with a 1 mol dm^{−3} pyridine solution did not show any interaction. Addition of undiluted pyridine to these dithiocar-

bamates also did not show any interaction. This behavior clearly indicates the reluctance of these dithiocarbamates to form adducts with monodentate bases because of higher electron density on Ni(II) centre.⁷ In the present study, the introduction of electronwithdrawing −CH₂CH₂OH groups in the place of −CH₂CH₃ groups did not induce adduct forming ability on the nickel(II) center. However, the presence of powerful electronwithdrawing substituents such as −CH₂CF₃ were shown to induce the adduct forming ability.⁴

Interaction with Ethylenediamine (en): The dithiocarbamate complexes showed varying extent of interaction with en. Addition of 1 mol dm^{−3} aqueous en to solid dithiocarbamates, II and III resulted in a clear pink colored solution, whereas, the diethyl analogue did not go into solution. Even on addition of undiluted en, the bis(diethyldithiocarbamato)nickel(II) did not show any interaction which showed the extraordinary stability associated with this complex. Interaction of Ni(II)–trimethylene bis(dithiocarbamate) complex with en was also investigated for a comparison. The behavior of this complex of stoichiometry (S₂CNHCH₂CH₂CH₂NHCS₂)Ni was identical with those of the complexes I, II, and III.

Electronic spectra of the pink solutions obtained were recorded with 1 mol dm^{−3} ethylenediamine as the reference. The spectra were identical with bands at 340, 550, and 900 nm characteristic of an octahedrally coordinated Ni(II). A similar electronic spectrum was obtained for a solution of Ni(NO₃)₂ in en which is nothing but [Ni(en)₃](NO₃)₂. Therefore, the pink-colored solutions obtained in both the cases were identified to contain the [Ni(en)₃]²⁺ chromophore. Addition of methanolic en solution 1 mol dm^{−3} to these dithiocarbamates results in a fine pink precipitate. When the precipitate was isolated it decomposed to the parent dithiocarbamate. The pink-colored aqueous solutions, on addition of HCl (2 equiv) precipitated the parent dithiocarbamates which clearly indicated the existence of the equilibrium,



It is obvious that in no case adduct formation was observed but a complete displacement of dtc[−] from the coordination sphere takes place.

The quantity of dithiocarbamates precipitated by the addition of HCl (2 equiv, 50 ml) to [Ni(en)₃](dtc)₂ (15

Table 1. Spectral Data and Lattice Parameters of $[\text{Ni}(\text{en})_3]\text{S}_2\text{O}_3$ Crystals Obtained by the Interaction of $\text{Ni}(\text{dtc})_2$ with Aqueous Ethylenediamine

Electronic spectral data		IR data		Lattice parameters
nm		cm^{-1}		
900	${}^3\text{A}_{2g} \rightarrow {}^3\text{T}_{2g}$	3270, 3150	$\nu_{\text{N-H}}$	Molecular formula: $\text{C}_6\text{H}_{24}\text{N}_6\text{O}_3\text{S}_2\text{Ni}$
550	${}^3\text{A}_{2g} \rightarrow {}^2\text{T}_{1g}$ (F)	1580	$\nu_{\text{N-H}}$ bend	Crystal: pink, rod-shaped
340	${}^3\text{A}_{2g} \rightarrow {}^3\text{T}_{1g}$ (P)	1450	$\nu_{\text{C-N}}$	Cell dimensions: $a=b=16.073$ (3) Å $c=9.871$ (4) Å Volume= 2208 Å ³ Crystal system=Hexagonal Space group= $P6_322$ Density= 1.58 g cm ⁻³

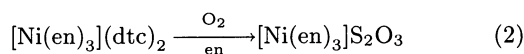
mmol, 10 ml) decreased as the solution was allowed to age. After two or three days pink-colored crystals separated from the solution. Elemental analysis of the pink crystals showed the Ni(II) to sulfur ratio to be 1 : 2 and analyzed to $[\text{Ni}(\text{en})_3]\text{S}_2\text{O}_3$. The presence of $\text{S}_2\text{O}_3^{2-}$ as the counter ion was also, proved by the reducing properties of the crystals towards iodine. When acidified iodine was added to the pink crystals directly there was immediate decolorization.

The infrared spectrum of $[\text{Ni}(\text{en})_3]\text{S}_2\text{O}_3$ crystals contained $\nu_{\text{N-H}}$ bands around 3270 and 3150 cm^{-1} . The splitting is due to N-coordination to metal. The N-H bending, $\nu_{\text{C-N}}$ and $\nu_{\text{C-C}}$ were observed at 1580, 1450, and 1270 cm^{-1} respectively. The S-O stretching bands appeared around 1000 and 1140 cm^{-1} . But a comparison of the IR spectra of $[\text{Ni}(\text{en})_3]\text{Cl}_2$ and $[\text{Ni}(\text{en})_3]\text{SO}_4$ were also identical. Hence IR spectra did not provide any conclusive evidence about the nature of the counter ion.

The crystals obtained by the interaction of Ni(II)dithiocarbamate complex with aqueous ethylenediamine were finally confirmed to be $[\text{Ni}(\text{en})_3]\text{S}_2\text{O}_3$ from lattice constants measurement. Lattice constants of the crystals determined using CAD4 diffractometer agreed well within the limits of experimental errors of the lattice parameters of the authentic $[\text{Ni}(\text{en})_3]\text{S}_2\text{O}_3$ crystals prepared. The lattice constants along with the electronic and IR spectral bands are listed in Table 1.

In the present study, the $\text{Ni}(\text{dtc})_2$ complexes in aqueous ethylenediamine, excepting the diethyl analogue, undergo complete displacement to form the $[\text{Ni}(\text{en})_3]^{2+}$ chromophore. A similar experiment carried out in the absence of oxygen, in an inert N_2 atmosphere showed the reprecipitation of $\text{Ni}(\text{dtc})_2$ from the $[\text{Ni}(\text{en})_3](\text{dtc})_2$ solution without any drastic changes in the quantities for over a period of a month. This clearly supports the aerial oxidation of dtc^- to $\text{S}_2\text{O}_3^{2-}$ which showed appreciable decrease in the quantities of $\text{Ni}(\text{dtc})_2$ precipitated by the addition of HCl within a few days. Transition metal ions such as Cu(II), Fe(II), and Ni(II) are known

to promote oxidation of sulfur compounds under basic medium.⁸⁾ One such instance is the oxidation of sulfides, thioamides and sulfur to SO_4^{2-} by Cu(II)/pyridine system. However, the mechanisms of these conversions are obscure.⁶⁾ Therefore, the oxidation of dtc^- to $\text{S}_2\text{O}_3^{2-}$ in the present study may be represented as,



Experimental

The nickel(II)dithiocarbamates were prepared by the addition of aqueous nickel(II) chloride solution to the freshly prepared $\text{R}_2\text{NCS}_2\text{Na}$ in methanol. The resulting complexes were filtered and recrystallized. The complexes analyzed to the formula $\text{Ni}(\text{dtc})_2$.

Aqueous and methanolic solutions of pyridine (1 mol dm⁻³, 50 ml), ethylenediamine (1 mol dm⁻³, 50 ml) were added to the solid dithiocarbamates (15 mmol) to study the interaction. All the reagents used were of analytical grade.

Electronic spectra were recorded on Varian Cary 2390 spectrophotometer and the infrared spectra were recorded on a Perkin-Elmer 257 spectrophotometer. The unit cell dimensions of the crystals were determined using an Enraf Nonius CAD4 diffractometer on a Cu $K\alpha$ source.

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