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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^-=dithiocarbamato anions) show interesting reactivity patterns in their reactions with Lewis bases. These complexes form mixed ligand complexes with PR_3 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 $S_2O_3{}^{2-}$ being the counter anion was tested. Even though infrared spectrum could not confirm the $S_2O_3{}^{2-}$ anion, the final confirmation came form the X-ray analysis of the authentic crystals. This is a rare occasion of metal ion catalyzed oxidation of S^{2-} to $S_2O_3{}^{2-}$ 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 $S_2O_3{}^{2-}$ in a basic solution. The following dithiocarbamates, (I) bis(diethyldithiocarbamato)nickel(II), $[(C_2H_5)_2NCS_2]_2Ni$; (II) bis[(2-hydroxyethyl)dithiocarbamato]nickel(II), $[(HOC_2H_4)HNCS_2]_2Ni$, and (III) bis[(bis(2-hydroxyethyl)dithiocarbamato)]nickel(II), $[(HOC_2H_4)_2NCS_2]_2Ni$; 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 dithiocarbamates 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 $-CH_2CH_2OH$ groups in the place of $-CH_2CH_3$ groups did not induce adduct forming ability on the nickel(II) center. However, the presence of powerful electronwithdrawing substituents such as $-CH_2CF_3$ 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 $(S_2CNHCH_2CH_2CH_2NHCS_2)Ni$ 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 $Ni(NO_3)_2$ in en which is nothing but $[Ni(en)_3](NO_3)_2$. 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,

$$Ni(dtc)_2 \overset{en}{\rightleftharpoons} [Ni(en)_3]^{2+}[(dtc)_2]^{2-} \qquad (1)$$

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 [Ni(en)$_3$] S_2O_3 Crystals Obtained by the Interaction of Ni(dtc)$_2$ with Aqueous Ethylenediamine

Electronic spectral data		IR data		Lattice parameters
nm		cm^{-1}		
900	$^3A_{2g}\rightarrow{}^3T_{2g}$	3270, 3150	ν_{N-H}	Molecular formula: $C_6H_{24}N_6O_3S_2Ni$
550	$^3A_{2g}\rightarrow{}^2T_{1g}$ (F)	1580	ν_{N-H} bend	Crystal: pink, rod-shaped
340	$^3A_{2g}\rightarrow{}^3T_{1g}$ (P)	1450	ν_{C-N}	Cell dimentions: $a=b=16.073$ (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 [Ni(en)$_3$]S_2O_3. The presence of $S_2O_3{}^{2-}$ 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 Ni(en)$_3S_2O_3$ crystals contained ν_{N-H} bands around 3270 and 3150 cm^{-1}. The splitting is due to N-coordination to metal. The N–H bending, ν_{C-N} and ν_{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 [Ni(en)$_3$]Cl_2 and [Ni(en)$_3$]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 [Ni(en)$_3$]S_2O_3 from lattice constants measurement. Lattice constants of the crystals determined using CAD4 diffractrometer agreed well within the limits of experimental errors of the lattice parameters of the authentic [Ni(en)$_3$]S_2O_3 crystals prepared. The lattice constants along with the electronic and IR spectral bands are listed in Table 1.

In the present study, the Ni(dtc)$_2$ complexes in aqueous ethylenediamine, excepting the diethyl analogue, undergo complete displacement to form the [Ni(en)$_3$]$^{2+}$ chromophore. A similar experiment carriedout in the absence of oxygen, in an inert N_2 atmosphere showed the reprecipitation of Ni(dtc)$_2$ from the [Ni(en)$_3$](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 $S_2O_3{}^{2-}$ which showed appreciable decrease in the quantities of Ni(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 $S_2O_3{}^{2-}$ in the present study may be represented as,

$$[Ni(en)_3](dtc)_2 \xrightarrow[en]{O_2} [Ni(en)_3]S_2O_3 \qquad (2)$$

Experimental

The nickel(II)dithiocarbamates were prepared by the addition of aqueous nickel(II) chloride solution to the freshly prepared R_2NCS_2Na in methanol. The resulting complexes were filtered and recrystallized. The complexes analyzed to the formula Ni(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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