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Ligand Alkylation of Bis(*N*,*N*-diethyldithiocarbamato)nickel(II) by α,α'-Dibromo-*o*-xylene[1]

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In recent years there has been considerable activity in the field of reactions of coordinated ligands and the use of these reactions in preparing macrocyclic complexes. Our interests in this area have led us to investigate the alkylation of bis(*N*,*N*-diethyldithiocarbamato)nickel(II) by α,α'-dibromo-*o*-xylene (DBX).

Busch and co-workers have investigated the reactivity of coordinated sulfur atoms with a variety of alkylating agents.[2-9] They observed that the sulfur atom remains bonded to the metal ion during S-alkylation.[3] Also, it has been possible to synthesize macrocyclic chelates through ligand reactions; successful macrocyclization was first attained using DBX.[10] Busch's group observed that in 1,2-dichloroethane relatively low yields of macrocyclic compounds were obtained and a tenfold excess of alkylating agent was required.[11]

In contrast to these macrocyclization reactions we have observed ligand removal on alkylation with the formation of dithiolium salts. This is very much like Tanaka and Abe's recent observation during the alkylation of dithiocarbamatoalkyltin(IV) compounds.[12]

Experimental Section

Physical Measurements. Electronic Spectra. A Cary Model 14 was used.

Thin-Layer Chromatography (TLC). All TLC plates (5 × 20 cm) were prepared using indicating silica gel, GF-254 (E. Merck Co., Darmstadt, Germany) with 0.25 mm thick layers activated by drying at 110°C for 1 h. Elution was accomplished using a mixed solvent containing equal volumes of chloroform and benzene. Fresh eluent was prepared every third day. All spots were visualized with both ultraviolet light (254 and 350 nm) and iodine staining. Standards were always eluted on the same plate as the sample.

Infrared Spectra. Spectra of the compounds from 700 to 3500 K were recorded on a Perkin-Elmer Infracord spectrophotometer. Mineral oil or halocarbon mulls were supported between sodium chloride or cesium bromide plates.

Spectra from 300 to 700 K were recorded on a Beckman IR-5-A CsBr spectrophotometer. Mulls were supported between cesium bromide plates.

Abbreviations used in reporting the absorption maxima are as follows: s, strong; m, medium; w, weak intensity; br, broad band maximum; sh, shoulder; v, very.

Magnetic Measurements. The Gouy method was used to determine magnetic susceptibilities[13] employing a Nobatron DCR 80-10 power supply and a Mettler semimicro balance. All samples were run at two field strengths (approximately 4 and 8 kOe) at room temperature ($Hg[Co(SCN)_4]$ standard[13]). Moisture-sensitive samples were put in the Gouy tube inside a glovebag under nitrogen. Values are corrected for ligand diamagnetism.[14]

Melting Points. A Thomas-Hoover Unimelt capillary melting point apparatus was used to determine the melting range of solid samples. Sealed capillaries were used for moisture-sensitive samples. All reported temperatures are uncorrected.

Elemental Analysis. Quantitative elemental analyses were performed by Baron Consulting Co., Orange, Conn. 06477.

Reagents. All chemicals were reagent grade and used as received unless otherwise noted. Bis(*N*,*N*-diethyldithiocarbamato)nickel(II), $[Ni(dtc)_2]$, was prepared using the method described by Durgaprasad et al.[15] Anal. Calcd for $NiS_4C_{10}H_{20}N_2$: C, 33.80; H, 5.67; N, 7.88; S, 36.12. Found: C, 33.82; H, 5.63; N, 7.88; S, 35.95.

Preparation of Benzo[*e*]-1,3-dithiepan-2-diethylimmonium Tribromooctachloropentanickelate(II), $xdtcNi_5Cl_8Br_3$. This preparation was performed many times with variation in DBX concentration and reflux time to assess their effect on the product. Atmospheric moisture must be excluded in all manipulations. In a typical sequence $Ni(dtc)_2$, 1.80 g (5.08 mmol) was dissolved in 250 ml of 1,2-dichloroethane and stirred for 0.5 h to ensure dissolution. α,α'-Dibromo-*o*-xylene, DBX, 13.26 g (50.5 mmol) in 100 ml of 1,2-dichloroethane, was added. This mixture was refluxed for 46 h (protected with Drierite), cooled to room temperature, and filtered (under argon) washing the peach-colored solid with at least two 25-ml portions of 1,2-dichloroethane. It was dried in vacuo over phosphorus pentoxide. The green filtrate was reserved for further investigation (below). Handling of the highly hygroscopic product was performed in a glovebag filled with argon or nitrogen; mp >275°C (color change to tan by 225°C).

A number of samples prepared in this fashion were analyzed and the formula was found to approximate $xdtcNi_5Cl_8Br_3$ (Table I).

Yields of $xdtcNi_5Cl_8Br_3$ were found to depend on both reflux duration and the mole ratio of reactants, $Ni(dtc)_2$ and DBX. Refluxing a tenfold excess of DBX with $Ni(dtc)_2$ in 1,2-dichloroethane for 8 h gave less than 1% yield. The other nickel-containing product, $(xdtc)_2NiBr_4$, could be obtained from the filtrate by solvent evaporation (contaminated with organic products). Increasing the reflux time to 23 h raised the yield of $xdtcNi_5Cl_8Br_3$ to about 83%; conversion was complete after 46 h.

$xdtcNi_5Cl_8Br_3$ is insoluble in nonpolar solvents and decomposes in polar solvents. Dissolution in water followed by the addition of $LiClO_4$ produced a white precipitate of $xdtcClO_4$ (dried in vacuo over P_4O_{10}); mp 173–174°C. Anal. Calcd for $C_{13}H_{18}NS_2ClO_4$: C, 44.37; H, 5.17; N, 3.98; S, 18.22; Cl, 10.07. Found: C, 44.27; H, 5.01; N, 4.26; S, 15.18; Cl, 10.57.

A proton NMR spectrum (deuterated DMSO) showed no paramagnetic or hydrogen containing organic impurities. Sharp peaks were observed at chemical shifts, δ, of 1.30 (triplet, $J = 7$ Hz), 4.05 (quartet, $J = 7$ Hz), 4.54 (singlet), and 7.42 (singlet). The spin–spin splittings and integrated intensities of 6:4:4:4, respectively, for the multiplets, indicate the structure of the cation $xdtc^+$ is as shown (**1**). Further evidence for this structure is the presence of the "thioureide" band at 1550 K in the infrared spectrum, typical of species containing the dithiocarbamate functional group.[16] Tanaka and Abe's[12] isolation of dithiolium salts from dithiocarbamates lends support to our choice of structure.

Infrared maxima (K) of $xdtcNi_5Cl_8Br_3$: 2900 (s), 1500 (m–s), 1450 (s), 1375 (m), 1340 (m), 1285 (m), 1270 (m), 1220 (w), 1182 (s), 1138 (m), 1090 (m), 1070 (m), 1060 (w, sh), 985 (m), 960 (w), 911 (w), 890 (w), 870 (w), 827 (w–m), 770 (s), 720 (vw), 667 (s), 586 (m), 465 (m).

Thin-layer chromatography of the filtrate (above) showed several species. A small amount of $Ni(dtc)_2$ remained; additionally the $xdtc^+$ ion, $NiBr_4^{2-}$ ion, and α,α'-dichloro-*o*-xylene (DCX) were found. Evaporation of solvent gave the expected mixture. The formation of DCX has been dealt with already.[17]

Another organic product in the filtrate was identified by fractional distillation of the 1,2-dichloroethane (25-cm Vigreux column) between 82 and 84°C. Mass spectrometry of the solution gave identifiable ions at m/e 142 ($ClCH_2CH_2Br^+$) and 108 ($CH_2CH_2Br^+$). These ions indicate the presence of 1,2-bromochloroethane.

When $Ni(dtc)_2$ and DCX were mixed (as above with DBX), the bulk of the reactants was unchanged indicating DCX to be considerably less reactive toward $Ni(dtc)_2$ than DBX.

Preparation of Bis(benzo[*e*]-1,3-dithiepan-2-diethylimmonium) Tetrabromonickelate(II), $(xdtc)_2NiBr_4$. $Ni(dtc)_2$, 0.30 g (0.85 mmol), in 60 ml of 1,2-dichloroethane was stirred under argon. DBX, 2.50

Table I. Elemental Analysis of $xdtcNi_5Cl_8Br_3$

Sample	% C	% H	% N	% S	% Cl	% Br	% Ni	Mol of halogen:5 mol of Ni
I	15.96	2.18	1.11	5.77	26.95	20.32	26.5	11.2
II	15.45	2.51	0.75	5.25	28.18	18.47	28.5	10.6
III	14.06	2.46	1.10	5.30	29.30	15.90	28.1	10.7
IV	14.80	1.92	1.67	6.11	27.43	19.81		
Av I–IV	15.06	2.26	1.16	5.61	27.96	18.62	27.7	10.8
$xdtcNi_5Cl_8Br_3$	14.60	1.70	1.31	6.00	26.52	22.41	27.4	11.0
$xdtcNi_5Cl_9Br_2$	15.32	1.77	1.37	6.26	31.13	15.59	28.6	11.0

g (9.5 mmol), in 20 ml of 1,2-dichloroethane was added. Deep blue $(xdtc)_2NiBr_4$ commenced crystallization within a few days. After 25 days the hygroscopic solid was filtered (under argon) and washed with 50 ml of 1,2-dichloroethane; then it was quickly transferred to a vacuum desiccator and dried in vacuo over phosphorus pentoxide; yield 15%; mp 165–167°C (no observable decomposition).

No chloride is present in the blue solid and all data indicate its empirical formula is $C_{26}H_{36}N_2S_4NiBr_4$. Anal. Calcd for $C_{26}H_{36}N_2S_4NiBr_4$: C, 35.55; H, 4.12; N, 3.17; S, 14.51; Br, 36.18; Ni, 6.65. Found: C, 35.19; H, 3.95; N, 3.30; S, 13.60; Br, 36.84; Ni, 5.27.

The electronic spectrum of $(xdtc)_2NiBr_4$ (mineral oil mull between quartz plates) (6.95, 13.2, 13.9, 32.6, and 42.0 kK) is similar to that of $[(C_2H_5)_4N]_2NiBr_4$ in the same type of mull (7.02, 13.1, and 14.0 kK).

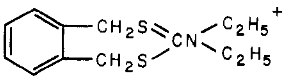
Infrared maxima (K): 2900 (s), 1525 (m–s), 1450 (s), 1365 (s), 1340 (m), 1290 (m–w), 1270 (m), 1210 (w), 1180 (m), 1145 (m), 1090 (m), 1055 (m), 990 (m), 872 (m), 850 (m), 835 (m), 790 (w), 762 (s), 715 (m, sh), 710 (s), 667 (s), 565 (m), 545 (m), 425 (s), 352 (w, br).

Sodium *N,N*-Diethyldithiocarbamate Trihydrate with *α,α'*-Dibromo-*o*-xylene in 1,2-Dichloroethane. Solutions of sodium *N,N*-diethyldithiocarbamate trihydrate, $Na(dtc)\cdot 3H_2O$, 3.27 g (14.5 mmol) in 30 ml of 1,2-dichloroethane, and DBX, 1.99 g (7.5 mmol) in 40 ml of 1,2-dichloroethane, were mixed and the flask was stoppered. Filtration, after 24 h, gave 1.34 g of sodium bromide.

The filtrate was refluxed for 66 h (protected from atmospheric moisture) and the resulting solution evaporated (vacuum). Two recrystallizations from ethanol gave white crystals. Elemental analysis and the mass spectrum are consistent with an empirical formula $C_{18}H_{28}N_2S_4$. Anal. Calcd for $C_{18}H_{28}N_2S_4$: C, 53.98; H, 7.05; N, 7.00; S, 31.97. Found: C, 54.31; H, 6.83; N, 6.51; S, 30.32.

Results and Discussion

Our original goal, to obtain a macrocyclic complex derived from $Ni(dtc)_2$, was not realized. Instead, ligand alkylation resulted in the formation of a new cation (xdtc) (**1**). As dithiocarbamate ligands were alkylated and removed from nickel, $NiBr_4^{2-}$ and the new ion $Ni_5Cl_8Br_3^-$ were formed resulting in the crystallization of their xdtc salts. Halide exchange between $NiBr_4^{2-}$ and 1,2-dichloroethane solvent was the source of chloride ion appearing in the product.



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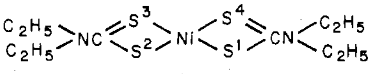
Dialkylation can occur at S^1 and S^2 or at S^1 and S^4 in $Ni(dtc)_2$ (**2**). Our isolated product indicates that the S^1 and S^4 sites are the preferential positions for attack under the conditions employed. Schrauzer and Rabinowitz also found that attack by alkyl halides occurred at the S^1 and S^4 positions in the bis(ethylenedithiolato)nickel(II) dianion (**3**).[18] These authors explained that the affinity of the second alkylating group for S^4 is due to an increased negative charge density on this atom, the nucleophilicity of S^4 thus increasing after alkylation of S^1 occurs. This effect is probably operative in our reaction as well, leading to the observed products.



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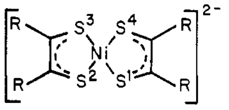

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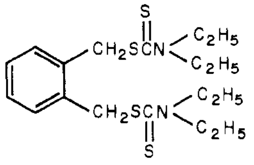
Dialkylation of S^1 and S^4 converts the coordinated thiolo groups into thioethers with a decrease in their ligand field strength.[19] This certainly facilitates replacement of xdtc in nickel's coordination sphere by halides. On the other hand, Schrauzer and Rabinowitz observed that dialkylation of the bis(ethylenedithiolato)nickel(II) dianion occurred without bond cleavage,[18] and Busch and co-workers found dialkylation of nickel(II) complexes containing two sulfur and two nitrogen donors did not cause cleavage but led to isolation of stable macrocyclic coordination compounds.[7,10,11]

Part of the reason for the observed instability of a complex thioether in the system under investigation is steric. Alkylation at S^1 and S^4 would affect the S–Ni–S bond angle and thus change sulfur's donor ability. It would be very interesting to attempt alkylation of Schrauzer and Rabinowitz's compounds with DBX and see if ligand cleavage occurs.

Prinzback and Futterer have recently reviewed the preparation and properties of known 1,3-dithiolium ions.[20] Our route to the formation of a 1,3-dithiolium ion is quite different from previously reported procedures, no earlier work having utilized a metal chelate in the synthesis. The importance of nickel is underscored by comparing the products obtained when sodium *N,N*-diethyldithiocarbamate, Na(dtc), is used in place of $Ni(dtc)_2$. Under similar conditions Na(dtc) and DBX in 1,2-dichloroethane yield **4**. One sulfur from each dtc moiety has been alkylated in contrast to the observed dialkylation of $Ni(dtc)_2$.



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From these results it is apparent that we are observing another example of the template effect;[21] the metal ion orients molecules and influences reaction rates in such a fashion that the obtained products are quite different from those produced in the absence of metal ion.

The present work was conducted in 1,2-dichloroethane since alkylation reactions are known to occur in this solvent.[6,10,11] (Interestingly, our reactions would not proceed in benzene.) A disadvantage of 1,2-dichloroethane is the fact that it is a potential reactant; the interaction of metal complexes with halogenated solvents has been observed on several occassions.[22,23] Thus, when nickel complexes containing chloride as well as bromide were isolated, the results were not entirely unexpected. The observed lack of reactivity toward $Ni(dtc)_2$ of the exchange product, DCX, accounts for the necessity of

Table II. Band Maxima, *Dq*, and *B* Values for Some Octahedrally Coordinated Nickel(II) Halide Compounds

Compd	σ_1	σ_2	σ_3[b]	*Dq*	*B*	Ref
$CsNiCl_3$	7.10	11.8	22.2	710	845	27
$NiCl_2$	7.40	12.8	21.8	740	780	27
$NiBr_2$	7.15	12.1	(20.3)[a]	715	695	27
$xdtcNi_5Cl_8Br_3$	7.08	11.8	21.4	708	787	This work

[a] Shoulder on a charge-transfer band. [b] Values in kK; *Dq* and *B* in K. σ_1 is the assigned transition $^3A_{2g} \rightarrow {}^3T_{2g}$; σ_2 is the assigned transition $^3A_{2g} \rightarrow {}^3T_{1g}(F)$; σ_3 is the assigned transition $^3A_{2g} \rightarrow {}^3T_{1g}(P)$. [c] Mineral oil mull between quartz plates.

using large excesses of DBX when alkylating complexes in chlorinated solvents.

Characterization of $xdtcNi_5Cl_8Br_3$ (most likely mixed with $xdtcNi_5Cl_9Br_2$) allows some generalizations concerning the structure of this new compound. The nickel ions appear to be octahedrally coordinated based on the electronic spectrum (Table II) and the magnetic moment of 3.54 BM/nickel (assuming the Curie law). This moment is quite in agreement with that observed for octahedral $CsNiCl_3$ (3.50 BM at 300 K).[24] Such a high value for the moment suggests a spin–orbit coupling constant of about −375 K.[25] An additional peak at 26.6 kK in the electronic spectrum of $xdtcNi_5Cl_8Br_3$ is assigned as a cation (xdtc) transition. Several known 1,3-dithiolium ions have adsorbances in the 25–42 kK range.[26]

When $Ni(dtc)_2$ and DBX were allowed to stand in 1,2-dichoroethane at room temperature, blue crystals of $(xdtc)_2NiBr_4$ appeared within several days. Analysis and the visible spectrum confirmed the nature of the anion in this salt. It was found to be the typical tetrahedral $NiBr_4^{2-}$ observed by others.[28]

Yields of $(xdtc)_2NiBr_4$ and $xdtcNi_5Cl_8Br_3$ are inversely related in that one appears to form at the expense of the other. At room temperature $(xdtc)_2NiBr_4$ is isolated while at reflux (and with longer reaction time) $xdtcNi_5Cl_8Br_3$ is the product. Thus it appears that $NiBr_4^{2-}$ is first formed and then interacts with 1,2-dichloroethane producing the ultimate product. No reaction is observed between $Ni(dtc)_2$ and 1,2-dichloroethane in the absence of DBX, while $(xdtc)_2NiBr_4$ with fresh 1,2-dichloroethane (reflux) forms $xdtcNi_5Cl_8Br_3$.

Thus, to summarize, we have a complex and interesting reaction between a chlorinated solvent and a nickel(II) complex. The reaction of $Ni(dtc)_2$ with DBX is different from reactions previously reported. Studies utilizing dithiocarbamato complexes of other metal ions should lead to some interesting products and further information concerning the metal–sulfur bond.

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Registry No. $(xdtc)Ni_5Cl_8Br_3$, 57594-29-3; $xdtcClO_4$, 57484-17-0; $(xdtc)_2NiBr_4$, 57527-41-0; $Ni(dtc)_2$, 14267-17-5; DBX, 91-13-4; 4, 57484-18-1; Na(dtc), 148-18-5.

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Effects of Quenchers on the Emission and Photoracemization of Tris(1,10-phenanthroline)chromium(III)

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The observation that several Cr(III) complexes of O_h and D_3 symmetries exhibit room-temperature solution phosphorescence[1] has assisted considerably in elucidating mechanistic details of their photochemistry. For the majority of these systems, selective doublet ^2E_g quenching agents have been found, thus enabling a distinction to be made between the quartet $^4T_{2g}$ and doublet ^2E_g as excited-state precursors to photochemical reaction.[2,3] The case of $Cr(phen)_3^{3+}$ (phen = 1,10-phenanthroline)[3] is of particular interest because of the marked influence of the medium on its photochemical and photophysical behavior.

We have previously discussed the highly efficient quenching of $(+)_{589}$-$Cr(phen)_3^{3+}$ phosphorescence and photoracemization in aqueous solution by iodide ion.[3] We have recently noted[4] the unusual emission behavior of $Cr(phen)_3^{3+}$ and the 2,2′-bipyridine analogue in dimethyl sulfoxide solution. In this note, we reexamine iodide quenching and extend our earlier discussion of the photoracemization of $(+)_{589}$-$Cr(phen)_3^{3+}$ in aqueous solution, based on an analysis of new quenching data for the anions SCN^- and OH^- and for molecular oxygen. The O_2 data elucidate and correct our earlier report. The OH^- data present an interesting mechanistic puzzle not yet resolved.

Experimental Section

$(+)_{589}$-$Cr(phen)_3(ClO_4)_3$ was isolated according to the literature method.[5] All other reagents used were of analytical grade quality. Stock solutions of the chloride salt used in the investigation were prepared by ion-exchange chromatography of the perchlorate salt using a Dowex 1-X4 resin (Cl^- form).

Racemization and luminescence data were collected using equipment described before.[1] The *T* dependence of phosphorescence