Sulfur Chelates. XVI. Chemical Properties of Oxidized Nickel(II) Dithiocarbamates. The X-Ray Crystal Structure of Tris(*N*,*N*-di-*n*-butyldithiocarbamato)nickel(IV) Bromide, $NiC_{27}H_{54}N_3S_6Br$[1]

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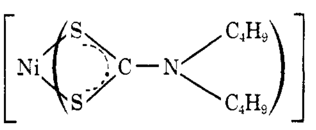
Received June 26, 1972

Abstract: The crystal and molecular structure of tris(*N*,*N*-di-*n*-butyldithiocarbamato)nickel(IV) bromide, Ni(*n*-Bu_2Dtc)$_3$Br (I), has been determined from three-dimensional X-ray data collected by counter methods. The structure has been refined to a final conventional *R* factor of 3.8% and a weighted *R* factor of 4.8% for 736 reflections with $I \geq 3\sigma(I)$. The system crystallizes in the space group D^2_{3d}-$P\bar{3}1c$ of the hexagonal system, with two formula units in a hexagonal cell of the dimensions $a = 14.386$ (3) and $c = 10.768$ (1) Å. The calculated density, 1.29 g/cm^3, agrees well with the measured density (flotation), 1.28 g/cm^3. The crystal consists of bromine ions arranged in a trigonal antiprismatic manner about columns composed of discrete, approximately D_3 symmetry, units of Ni(*n*-Bu_2Dtc)$_3^+$. The NiS_6 core is twisted by 45.4° from a trigonal prismatic arrangement. Both nickel and bromine possess D_3(32) site symmetry. The Ni–S bond measures 2.261 Å, the S–C bond is 1.708 Å, and the C–N bond distance is 1.318 Å. The "bite" distance, S···S, measures 2.794 Å. The nickel atoms along the columns are separated by 5.384 Å. The brown color of the Ni(*n*-Bu_2Dtc)$_3^+$ cation is found to photochemically and thermally bleach in CH_3CN and related solvents in a reversible manner. With stronger bases, the bleaching is irreversible. The products of bleaching are identified to be thiuram disulfide and nickel(II) species. The kinetics of the re-formation of Ni(*n*-Bu_2Dtc)$_3^+$ after bleaching in CH_3CN have been followed. The debleaching process is found to conform to a rate expression which is dependent on the square of the concentration of the bleached nickel and inversely proportional to the concentrations of thiuram disulfide and Br^-.

The synthesis by Brinkhoff[2] of Ni(*n*-Bu_2Dtc)$_3$Br (I) and related complexes[3] prompted us[4] to examine the physical properties and structures of these unusual materials. As implied by the title of this paper, the Brinkhoff–Steggerda formulation of Ni(*n*-Bu_2Dtc)$_3$Br as a nickel(IV) species is shown to be acceptable from a structural viewpoint. The chemical properties and, in particular, the photochromic behavior of the complex also confirm this hypothesis in the sense that reduction to nickel(II) can be achieved at the expense of ligand oxidation only with energy input. The dithiocarbamate ligand clearly plays an important role in stabilizing metal ions[5,6] in high oxidation states. This property of dithiocarbamates appears relevant to the known pharmacological and fungicidal activity of these species.[7]



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Experimental Section

All chemicals and solvents used in syntheses were reagent grade unless otherwise specified. Spectral grade solvents were obtained from Matheson Coleman and Bell, as were the di-*n*-butylamine and dibenzylamine. Analyses were performed by Galbraith Laboratories, Knoxville, Tenn., or by Crobaugh Laboratories, Cleveland, Ohio, as indicated. Chloroform-*d* was obtained from Columbia Organic Chemicals and was dried over $CaSO_4$ and filtered before use.

Physical Measurements. Electronic spectra were obtained on a Cary 14 spectrophotometer using matched quartz cells. Infrared spectra from 4000 to 625 cm^{-1} were recorded on a Perkin-Elmer 257 spectrophotometer. Far-infrared spectra were obtained from 900 to 300 cm^{-1} on a Beckman 5-A spectrophotometer. Proton magnetic resonance (pmr) spectra were obtained on Varian A-60, A60A, and HA-100 nuclear magnetic resonance spectrometers.

Conductivity data were obtained using a cell containing two curved platinum electrodes and a Leeds and Northrup 4866 Wheatstone bridge. The cell temperature was maintained at 25.0° using a Forma-Temp constant-temperature bath. Distilled water was obtained from Puritas and gave a conductance of 2.45×10^{-6} mho. A cell constant of 1.26 was obtained using a 0.0200 *M* potassium chloride solution as standard.[8] Nitromethane was purified from spectral grade by the method of Olah, *et al.*,[9] and gave a conductance of 4.27×10^{-6} ohm^{-1}. All values for the complex were obtained in a darkened room.

The acetonitrile used for kinetic studies was purified by the method of Perrin, Amarego, and Perrin.[10] Reagent grade pyridine was fractionally distilled from barium oxide before use. Spectral grade acetonitrile used for conductance measurements was dried over molecular sieves (Linde Type 4-A) and gave a conductance of 1.65×10^{-6} ohm^{-1}.

Magnetic susceptibility measurements were made on a Gouy-

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[1] Abstracted in part from the Ph.D. Thesis of R. G. F.

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[3] Abbreviations used: *n*-Bu_2Dtc = *N*,*N*-di-*n*-butyldithiocarbamate; Bz_2Dtc = *N*,*N*-dibenzyldithiocarbamate; Et_2Dtc = *N*,*N*-diethyldithiocarbamate.

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[6] P. T. Beurskens, H. J. A. Blaauw, J. A. Cras, and J. J. Steggerda, *Inorg. Chem.*, 7, 805, 810 (1968).

[7] G. D. Thorn and R. A. Ludwig, "The Dithiocarbamates and Related Compounds," Elsevier, Amsterdam, 1962.

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[9] G. A. Olah, S. J. Kuhn, S. H. Flood, and B. A. Harden, *J. Amer. Chem. Soc.*, **86**, 1043 (1964).

[10] D. D. Perrin, C. F. Amarego, and W. R. Perrin, "Purification of Laboratory Materials," Pergamon Press, New York, N. Y., 1966.

type set-up using double-ended tubes. Static-free conditions were obtained by use of a "polonium" brush. Measurements at four different field strengths were made using a Varian Model V-4000A electromagnet with a Varian Model V-2300A power supply and V-2301A current regulator. Mercury(II) tetrathiocyanatocobaltate(II) and tris(ethylenediamine)nickel(II) thiosulfate were used as standards.

A Varian E-3 electron paramagnetic resonance spectrometer was used for all epr spectra. Resonance spectrometers for pmr and epr measurements were equipped with a Varian V-4540 temperature controller. Temperatures are accurate to ±3°. Dimethyl-d_6 sulfoxide was obtained from Merck Sharp and Dohme. All other reagents and apparatus are as previously described.

Temperature control on the Cary 14 spectrometer was maintained using a constant-temperature block in the sample compartment and a Forma-Temp constant-temperature bath. Temperature calibration was made with a Meylan 204-D stopwatch and the recorder output of the Cary 14.

Rapid scan spectrophotometric measurements were made on an apparatus designed by Dr. T. Kuwana with the aid of Dr. G. Gruver, using 5-sec scans.

Preparations of Compounds. The diethylammonium salt of *N*,*N*-diethyldithiocarbamate was prepared by the reaction of diethylamine and carbon disulfide in petroleum ether (bp 30–60°). The product was isolated by filtration, washed with petroleum ether, and air-dried.

The potassium salts of *N*,*N*-dibenzyldithiocarbamate and *N*,*N*-di-*n*-butyldithiocarbamate were prepared by reaction of 1 equiv of carbon disulfide with a water solution containing 1 equiv each of the amine and potassium hydroxide. K(Bz$_2$Dtc) could be isolated as white crystals by cooling of the water solution in an ice bath. K(*n*-Bu$_2$Dtc) was not isolated.

N,*N*,*N*′,*N*′-Tetraethyl- and tetrabenzylthiuram disulfides were prepared by the method of von Braun[11] by the oxidation of the corresponding dithiocarbamate salt with iodine in ethanol.

Bis(dialkyldithiocarbamato)nickel(II) Complexes. These complexes were prepared by the general method of Cavell and Sugden[12] by reaction of the dithiocarbamate salts with nickel chloride in water solution. Ni(Et$_2$Dtc)$_2$ was recrystallized from acetone, Ni(Bz$_2$Dtc)$_2$ from methylene chloride–petroleum ether, and Ni(*n*-Bu$_2$Dtc)$_2$ from carbon tetrachloride–petroleum ether.

Tris(*N*,*N*-Di-*n*-butyldithiocarbamato)nickel(IV) Bromide, Ni(*n*-Bu$_2$Dtc)$_3$Br. This complex was prepared by the method of Brinkhoff[2] by the oxidation of Ni(*n*-Bu$_2$Dtc)$_2$ with bromine in carbon tetrachloride. The solid was removed from the carbon tetrachloride by filtration, stirred with water for 4 hr, filtered, and allowed to air-dry. The crude product was recrystallized from acetone, washed repeatedly with carbon tetrachloride and then with petroleum ether, and vacuum dried, mp 149–151°.

Anal. (Crobaugh Laboratories) Calcd for BrC$_{27}$H$_{54}$N$_3$NiS$_6$: C, 43.14; H, 7.24; Ni, 7.8. Found: C, 43.41; H, 7.51; Ni, 7.5.

The material is quite soluble in most polar organic solvents and seems stable indefinitely in dry chloroform. The crystalline material used in studies of this complex was stored in a vacuum desiccator over Drierite; however, materials stored in air showed no visible signs of decomposition over long periods of time.

Tris(*N*,*N*-dibenzyldithiocarbamato)nickel(IV) Bromide, Ni(Bz$_2$Dtc)$_3$Br. Ni(Bz$_2$Dtc)$_2$ (25.2 g, 0.036 mol) was partially dissolved in 300 ml of chloroform. To this was added 1.54 ml (0.024 mol) of bromine in about 50 ml of chloroform. A dark red-brown solution developed which was stirred for 1 hr and then gravity filtered and evaporated. The residue was recrystallized from spectral grade acetonitrile–anhydrous ether to give hexagonal prisms, dec pt 140°. From the analysis the final recrystallization apparently incorporated 1 mol of chloroform per mole of complex into the crystal. An attempt to obtain the material free of chloroform by heating under vacuum at 80° over P$_2$O$_5$ gave a product which analyzed poorly for the complex.

Anal. Calcd for BrC$_{45}$H$_{42}$N$_3$NiS$_6$·HCCl$_3$: C, 51.38; H, 4.03; N, 3.91; S, 17.89. Found: C, 51.03; H, 4.15; N, 4.48; S, 17.79.

This complex is soluble to some extent in most polar organic solvents, but is rather sensitive to moisture, especially in solution. The crystalline material was stored in a vacuum desiccator over CaSO$_4$.

Tris(*N*,*N*-di-*n*-butyldithiocarbamato)nickel(IV) Bromotrifluoroborate, Ni(*n*-Bu$_2$Dtc)$_3$BF$_3$Br. Ni(*n*-Bu$_2$Dtc)$_3$Br (1.5 g) was dissolved in 100 ml of spectral grade chloroform. To this solution was added 0.55 ml of 98% boron trifluoride etherate. The solution was stirred for 1 hr. Carbon tetrachloride (300 ml) was added and the solution cooled. Filtration gave about 1 g of crystalline product, which was washed with petroleum ether (bp 30–60°) and vacuum dried. The product was identified by its infrared spectrum, mp 107–110°.

Tris(*N*,*N*-di-*n*-butyldithiocarbamato)nickel(IV) Nitrate, Ni(*n*-Bu$_2$Dtc)$_3$NO$_3$. Ten grams (0.026 mol) of Ni(*n*-Bu$_2$Dtc)$_2$ was dissolved in 80 ml of spectral grade chloroform, and 3.4 ml (0.05 mol) of concentrated nitric acid was added. A vigorous reaction took place, and N$_2$O$_4$ was evolved from the solution.[13] When reaction had ceased, the mixture was cooled in an ice bath and sodium carbonate solution was added. The layers were separated and the chloroform layer was dried over CaSO$_4$. The solution was filtered and 200 ml of carbon tetrachloride was added. The solution was cooled and filtered again. About 2 g of black crystalline material was obtained, mp 108–109° dec. The product was identified by its infrared spectrum.

Tris(*N*,*N*-diethyldithiocarbamato)nickel(IV) Bromide, Ni(Et$_2$Dtc)$_3$Br. Ni(Et$_2$Dtc)$_2$ (3.5 g, 0.01 mol) was dissolved in 150 ml of chloroform. To this solution was added 1 g of bromine (0.06 mol) in 50 ml of chloroform. A dark red-brown solution developed and a pale yellow-green precipitate was formed. The solution was filtered and 300 ml of carbon tetrachloride was added. Filtration gave about 2 g of crystalline material, dec pt 90°. Attempts to further purify this complex resulted in extensive decomposition of the material to the Ni(Et$_2$Dtc)$_2$ complex (identified by its infrared spectrum). No sample suitable for analysis was obtained. Comparison of the visible spectrum of the crude product with that obtained for the Ni(*n*-Bu$_2$Dtc)$_3$Br complex in acetonitrile suggested the formation of Ni(Et$_2$Dtc)$_3$Br. In addition, the material obtained shows the same type of photobleaching (*vide infra*) observed for the other Ni(L$_2$Dtc)$_3$Br complexes.

In an alternate preparation, 15 g (0.05 mol) of (Et$_2$Dtc)$_2$ and 8 g (0.03 mol) of nickel bromide trihydrate were placed in 75 ml of tetrahydrofuran and stirred for 1 hr. The solution became dark red-brown during stirring. The solution was filtered, 200 ml each of ether and carbon tetrachloride were added, and the solution was cooled. Filtration gave about 3 g of a black powder. The infrared spectra (Nujol mulls) of the materials obtained in the two preparations were identical.

Preparation of Ni(*n*-BuDtc)$_3^+$ with Various Oxidizing Agents. Besides the halogens and thiuram disulfides reported by Brinkhoff[2] and concentrated nitric acid reported above, a number of other oxidizing agents have been found to react with Ni(*n*-Bu$_2$Dtc)$_2$ to yield Ni(*n*-Bu$_2$Dtc)$_3^+$. In these preparations the cation was identified by its very deep red-brown color and its characteristic photochromic interaction with light in coordinating solvents. The materials were not isolated and in most cases presumably contain a mixture of anions. Since the cation does not show photobleaching in chloroform, spectral grade acetone was used to sensitize these solutions to light.

N-Bromosuccinimide and *m*-chloroperoxybenzoic acid were found to react instantaneously with Ni(*n*-Bu$_2$Dtc)$_2$ in chloroform to yield Ni(*n*-Bu$_2$Dtc)$_3^+$. Na$_2$Cr$_2$O$_4$·H$_2$O in acetone and sodium chlorate in a 50% acetone–50% ethanol mixture also react with Ni(*n*-Bu$_2$Dtc)$_2$ if acid is added. Sulfuric acid was used in acetone and hydrochloric acid in the ethanol–acetone mixture. Ni(*n*-Bu$_2$Dtc)$_2$ dissolved in hexachloroacetone also oxidizes to Ni(*n*-Bu$_2$Dtc)$_3^+$.

Methods of Obtaining Kinetic Data. Photochemical bleaching of solutions of Ni(*n*-Bu$_2$Dtc)$_3$Br was studied spectrophotometrically using a light-pipe apparatus. The apparatus consisted of a 0.5-in. diameter L-shaped Lucite rod fitted through a metal plate which covered the sample compartment of the Cary 14. The Lucite rod could be moved vertically and positioned in front of the cell used. A metal cover, which fitted over the Lucite rod, made the sample compartment light tight. This apparatus allowed the use of a 150-W Harmony House projection flood lamp for photochemical bleaching, with minimum heating of the sample. A pair of 1-cm path-length round cells was used which had a diameter of $^7/_8$ in.

To study the spectrum and the kinetics of the formation of Ni(*n*-Bu$_2$Dtc)$_3^+$, an acetonitrile solution of Ni(*n*-Bu$_2$Dtc)$_3$Br was placed in the constant-temperature block of the Cary 14 and the

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(11) J. von Braun, *Ber.*, 35, 3368 (1902).

(12) H. J. Cavell and S. Sugden, *J. Chem. Soc.*, 621 (1935).

(13) Thiuram disulfides also react with acidified nitrates to produce N$_2$O$_4$ in THF.

light-pipe apparatus placed in position. The cell was allowed to thermally equilibrate in the dark for at least 12 hr. At the end of this time a visible spectrum of the solution was obtained. With the spectrophotometer shutter closed, the light pipe was lowered into position, and the top of the Lucite rod was illuminated with the photoflood lamp for 3 min. At the end of this time the light was turned off and the stopwatch started. This time was assumed to be t_0. The light pipe was withdrawn from the sample compartment and covered, and the spectrometer was activated.

Plots of absorbance *vs.* time were recorded at 5575 Å. This wavelength was chosen because of the very small absorbance (less than 1.5% of the unbleached solution) of the bleached solution.

Measurements of the change in absorbance in the near-infrared region were taken with 5-cm matched cells and a relatively concentrated solution of the complex. Since limited bleaching occurred in these solutions using the light pipe, bleaching was done outside the spectrophotometer.

In the measurement of the rate of formation of $Ni(Bu_2Dtc)_3^+$ by conductance, a solution of the $Ni(n\text{-}Bu_2\,Dtc)_3Br$ solution in acetonitrile was made up in a darkened room. The conductance of the solution (4.927×10^{-4} mol $l.^{-1}$) was obtained at 25.0° and this value was used for the conductance of the complex. The solution was then subjected to photoflood light until little or no brown color remained in the solution. The time of switching off the light was used as zero time. The conductance of the solution, which fell from a value of 5.25×10^{-5} ohm^{-1} to about 3.2×10^{-5} ohm^{-1}, was taken at 30-sec intervals.

X-Ray Crystallographic Structural Data. A large batch of the black crystals of $Ni(n\text{-}Bu_2Dtc)_3Br$ was examined under a microscope. Most crystals resembled hexagonal prisms and in general were not very well formed. Many crystals were examined on the Weissenberg camera and were found to be severely fractured. At all times the crystals were placed inside glass capillaries, partly because of sensitivity to moisture but primarily because the crystals dissolved slightly in common adhesives used to mount crystals on glass rods. After finding a good crystal, a complete series of Weissenberg and Buerger precession photographs was obtained which suggested trigonal symmetry. The systematic extinctions observed, hhl, $l = 2n + 1$, in the reciprocal lattice of $\bar{3}m$ Laue symmetry, are consistent only with the space group $D^2{}_{3d}\text{-}P\bar{3}1c$ (No. 163).

A crystal of $Ni(n\text{-}Bu_2Dtc)_3Br$, cut with a razor blade to a suitable size (roughly $0.3 \times 0.6 \times 0.1$ mm, the short distance being along the c axis), was chosen for data collection. The lattice parameters obtained from a least-squares fit to angular settings of 11 carefully centered reflections, high 2θ ($2\theta_{av} = 88.0°$), with takeoff angle of 1.5°, on a Picker automatic X-ray diffractometer, are $a = 14.386$ (3) and $c = 10.768$ (1) Å. The density, by flotation using cyclohexane and CCl_4, is 1.283 (8) g cm^{-3} (calculated, $Z = 2$, 1.293 g cm^{-3}). The two Ni atoms must occupy positions with $\bar{3}$ or 32 site symmetry.

Collection and Reduction of Intensity Data. Cu Kα radiation ($\lambda_{K\bar{\alpha}}$ 1.5418 Å), filtered by a nickel foil (0.241 mm), was used. Data were collected by the θ–2θ scan technique at a rate of 2°/min out to a maximum sin θ/λ of 0.594. In this manner, 1349 symmetry-independent reflections ($h \geq k \geq (-h/2)$, $l \geq 0$; $F_{hk0} = F_{h+k,\bar{k},0}$) were collected ($^1/_{12}$ of the total sphere of reflection). The crystal was mounted on a eucentric goniometer head such that the (520) diffraction vector was colinear with the ϕ axis of the four-circle diffractometer, in order to minimize the effect of multiple reflections.[14] A takeoff angle of 3.5° was used during data collection.

The intensities of three reflections in different parts of the reciprocal lattice were monitored as standards roughly every 50 reflections. No appreciable decomposition was observed. The greatest single deviation of any of the standard reflections from its mean was less than 3%.

The linear absorption coefficient for the Cu radiation, 51.05 cm^{-1}, along with the large size of the crystal, suggested that absorption corrections were desirable. Using ABSCOR, transmission coefficients obtained range from 0.28 to 0.46. The data were corrected for Lorentz and polarization effects [$1/Lp = 2 \sin 2\theta/(1 + \cos^2 2\theta)$]. The measured intensity was defined as

$$I = C_{scan} + 4.5 - \frac{t_{scan}}{2t_{bk}}(C_{bk1} + C_{bk2} + 9.0)$$

where C_{scan} refers to the counts during the scan (scan widths ranged from 2.2 to 3.4°), t_{scan} is the time interval of the scan, t_{bk} refers to the time interval for each stationary background measurement (20 sec), and C_{bk1} and C_{bk2} are the background counts at low and high ends of the scan range, respectively. Since the last figure in the counts punched out by the diffractometer system is truncated, the data reduction program used multiplies all the decacounts by ten and adds 4.5, a statistical average value as a result of the truncation.

Reflections were considered observed when

$$\frac{C_{scan} + 4.5}{(t_{scan}/2t_{bk})(C_{bk1} + C_{bk2} + 9.0)} \geq 1.2$$

With this criterion a full data set consisted of 964 reflections. The standard deviation in the intensity was defined as

$$\sigma(I) = [C_{scan} + 9.0 + (t_{scan}/2t_{bk})^2 \times (C_{bk1} + C_{bk2} + 18.0) + (pI)^2]^{1/2}$$

The constants 9.0 and 18.0 arise from truncation errors.[15] The constant p, chosen as 0.02, can be ascribed to errors in intensities when counting statistics are negligible, as in the case of high-intensity reflections. Of the 964 reflections in the full data set, 736 have $I \geq 3\sigma(I)$.

The raw data were checked for any systematic dependence of the difference between the low- and high-angle backgrounds as a function of 2θ in the manner described by Cotton and Pipal.[16] No dependence was found.

Solution and Refinement of the Structure. Initially a structure factor calculation was performed using the coordinates given to us by Beurskens.[17] The conventional R_1 factor [$R_1 = \Sigma||F_o| - |F_c||/\Sigma|F_o|$] turned out as 0.57. Disagreements between the calculated and observed structure factor amplitudes were extraordinarily large, so no refinement was attempted.

A Patterson Fourier calculated with the full data set readily revealed the positions of the Br–Br, Ni–Br, and Ni–Ni peaks. One of the Ni–S peaks was identified with reasonable certainty.

Structure factor calculations with several reasonable positions of C1 and N along with the coordinates of Ni, Br, and S deduced from the Patterson synthesis produced an R_1 of 0.42 and suggested that C1 and N occupy position (h) with twofold site symmetry. Ni was assumed to occupy the position a at $00^1/_4$ and Br was assumed to be in position c at $^1/_3$ $^2/_3$ $^1/_4$, both having 32 site symmetry.

Refinement was initiated, using a full-matrix least-squares procedure with isotropic temperature factors. Fourier synthesis at various stages of refinement revealed the positions of all the subsequent nonhydrogen atoms. With the full data set the refinement converged to an R_1 of 0.110 and a weighted R_2 [$R_2 = \{\Sigma w(|F_o| - |F_c|)^2/\Sigma w|F_o|^2\}^{1/2}$] of 0.130.

The atomic scattering factors for the nonhydrogen atoms were taken from Cromer and Waber.[18] Those used later for the hydrogen atoms were from Stewart, *et al.*[19] Cromer's values[20] for real and imaginary components of the anomalous dispersion correction to the atomic scatter factors were incorporated for Ni, S, and Br. Initially, a charge of +4 was assumed on nickel and the respective values for the scatter factors were extrapolated from Ni(III), using Co(II) to Co(III) scaling. Sulfur atoms were assumed to have a charge of $-^1/_2$ and bromine atoms were assumed to be Br(-1); all other atoms were considered neutral.

Anisotropic thermal parameters were introduced for all nonhydrogen atoms. An empirical weighting scheme of the Cruickshank[21] type was devised from a plot of average $|F_o|$ from a group of reflections against the average $[(|F_o| - |F_c|)^2]^{1/2}$ for that group. After three least-squares cycles, R_1 and R_2 converged to 0.066 and 0.081, respectively. A difference Fourier suggested the positions of the methylene hydrogen atoms, which were placed assuming

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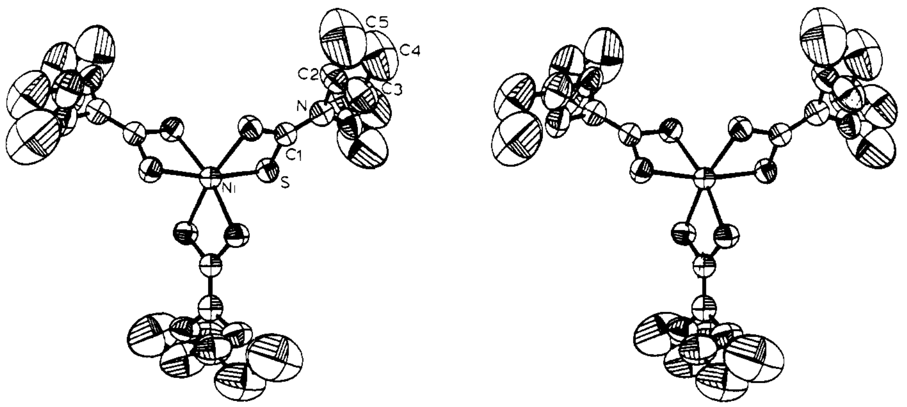

Figure 1. A stereopair presentation of the structure of the $Ni(n\text{-}Bu_2Dtc)_3^+$ cation.

Table I. Positional Parameters for $Ni(S_2CN(C_4H_9)_2)_3Br$

Atom	x	y	z
Ni	0	0	$^1/_4$
Br	$^1/_3$	$^2/_3$	$^1/_4$
S	0.1229 (1)	−0.0198 (1)	0.3599 (1)
C1	$(^1/_2 y)$	0.2215 (5)	$^1/_4$
N	$(^1/_2 y)$	0.3273 (5)	$^1/_4$
C2	0.2467 (6)	0.3874 (5)	0.1554 (6)
C3	0.2027 (7)	0.4132 (6)	0.0443 (7)
C4	0.2910 (10)	0.4816 (8)	−0.0529 (9)
C5	0.3214 (8)	0.4190 (6)	−0.1204 (5)
H21	0.288 (5)	0.353 (6)	0.138 (6)
H22	0.301 (6)	0.442 (7)	0.194 (6)
H31	0.136 (5)	0.342 (6)	0.011 (6)
H32	0.170 (6)	0.463 (6)	0.081 (6)
H41[a]	0.300	0.580	0.040
H42[a]	0.350	0.580	0.010
H51[a]	0.260	0.380	0.090
H52[a]	0.400	0.470	−0.090
H53[a]	0.38	0.500	−0.170

[a] Position fixed.

Table II. Thermal Parameters and Esd's[a] for $Ni(n\text{-}Bu_2Dtc)_3Br$

Atom	β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
Ni[b]	(β_{22})	0.0065 (1)	0.0089 (1)	$(^1/_2\beta_{22})$	0	0
Br[b]	(β_{22})	0.0079 (1)	0.0190 (2)	$(^1/_2\beta_{22})$	0	0
S	0.0078 (1)	0.0084 (1)	0.0095 (1)	0.0046 (1)	−0.0012 (1)	−0.0014 (1)
C1[b]	(β_{22})	0.0073 (3)	0.0101 (6)	$(^1/_2\beta_{22})$	0	0
N[b]	(β_{22})	0.0088 (3)	0.0120 (6)	$(^1/_2\beta_{22})$	0	0
C2	0.0112 (6)	0.0079 (4)	0.0145 (7)	0.0031 (4)	0.0032 (5)	0.0009 (5)
C3	0.0156 (8)	0.0115 (6)	0.0152 (8)	0.0047 (6)	0.0019 (6)	0.0013 (6)
C4	0.0302 15)	0.0151 (9)	0.0237 (13)	0.0086 (10)	0.0125 (2)	0.0025 (9)
C5[c]	0.0439 (22)	0.0290 (15)	0.0380 (19)	0.0226 (16)	0.0216 (17)	0.0101 (15)

Root-Mean-Square Displacements of the Atoms along the Principal Axes of the Thermal Ellipsoids (in Å)

Atom	r_1	r_2	r_3	Atom	r_1	r_2	r_3
Ni	0.226	0.226	0.230	C2	0.227	0.279	0.346
S	0.223	0.235	0.271	C3	0.280	0.314	0.383
C1	0.239	0.239	0.243	C4	0.299	0.349	0.560
N	0.262	0.262	0.266	C5	0.330	0.469	0.671
Br	0.250	0.250	0.335				

[a] The form of thermal ellipsoid is $\exp[-(\beta_{11}h^2 + \beta_{22}k^2 + \beta_{33}l^2 + 2\beta_{12}hk + 2\beta_{13}hl + 2\beta_{23}kl)]$. [b] Symmetry relations among coefficients of the anisotropic temperature factor are discussed by H. A. Levy (*Acta Crystallogr.*, **9**, 679 (1956)). [c] H21, H23, H31, H32 converged to $8.4 < B < 10.1$. For other H atoms $B > 16$.

tetrahedral angles and C–H bond lengths of 1.00 Å. The methyl proton positions were assumed to be staggered relative to the bonds on the adjacent methylene carbon atom. The calculated hydrogen positions were included in the refinement model, and their positional and isotropic thermal parameters were varied. Using the full data set R_1 converged to 0.051 and R_2 converged to 0.054. A difference Fourier indicated consistent positive density (~0.4) in the vicinity of Ni and negative density (~ −0.3) in S positions.

Instead of using the full data, the $I/\sigma(I) \geq 3$ data were selected at this point and the charge on Ni was assumed to be +1, while S atoms were considered neutral. A new Cruickshank weighting scheme was introduced. With a few cycles of refinement R_1 converged to 0.038 and R_2 converged to 0.048. The positions of the methyl hydrogen atoms were kept fixed in the calculated positions with a B of 20 Å^2. The other hydrogens with the exception of H42 and H41, which were subsequently fixed, converged to reasonable locations.

The final error in an observation of unit weight was 0.89 $[(N_o - N_r)^{-1}\Sigma w(|F_o| - |F_c|)^2]^{1/2}$. The final weighting scheme can be described by $\sigma(F_o) = 2.795 - 0.296|F_o| + 0.012|F_o|^2$, for $|F_o| \leq 11.4$, and $\sigma(F_o) = 0.896 + 0.019|F_o|$, for $|F_o| > 11.4$. In the last refinement cycle the largest shift over error in positional parameters of nonhydrogen atoms is 0.15, corresponding to the Z of C4 and related to a shift of 0.005 Å by the atom. The largest anisotropic thermal parameter shift is also in C5 corresponding to a shift over error value of 0.43 in β_{13}. The largest shift over error for the hydrogen atoms varied (H21, H22, H31, H32) is 0.23 for x of H21. This corresponds to a shift of the atom by 0.017 Å. The final difference Fourier reveals the largest residual density as 0.74 e/Å^3 in the vicinity of nitrogen atoms. Three hydrogen atoms did not refine well with isotropic thermal parameters. Aside from these, only spurious densities ranging from about −0.20 to +0.20 e/Å^3 were found. (A residual of 0.73 e/Å^3 near C5 may indicate a misplaced methyl hydrogen atom.)

Results

Description of the Structure of $Ni(n\text{-}Bu_2Dtc)_3Br$. The positional and thermal parameters obtained from the

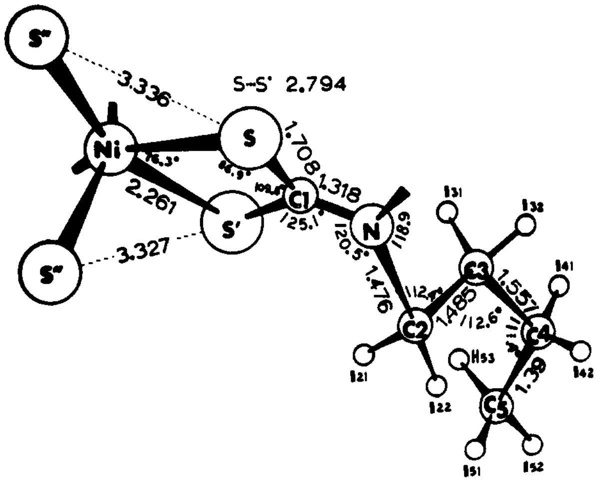

Figure 2. The geometric features of a portion of the Ni(n-Bu_2Dtc)$_3^+$ cation.

refinement of Ni(n-Bu_2Dtc)$_3$Br are listed in Tables I and II.[22] Figure 1 is a stereopair drawing of the cation. Table III lists the calculated bond distances and angles.

Table III. Bond Distances (Å) and Bond Angles (deg) for $Ni(S_2CN(C_4H_9)_2)_3Br$

	Bond Distances (esd)		
Ni-S	2.261 (1)	C2-H21	0.97 (1)
S-C1	1.708 (5)	C2-H22	0.89 (7)
C1-N	1.318 (8)	C3-H31	1.06 (7)
N-C2	1.476 (6)	C3-H32	1.10 (7)
C2-C3	1.485 (10)		
C3-C4	1.557 (11)		
C4-C5	1.388 (16)		
	Bond Angles (esd)		
S-Ni-S	76.33 (6)	N-C2-C3	112.4 (6)
Ni-S-C1	86.9 (1)	C2-C3-C4	112.6 (8)
S-C1-S	109.8 (4)	C3-C4-C5	111.4 (10)
S-C1-N	125.1 (1)	C2-N-C2'	118.9 (7)
C1-N-C2	120.5 (4)		
	Torsional Angle (esd)		
S-C1-N-C2		4.4 (6)	

The calculation of the estimated errors in these quantities incorporates correlations between parameters. The x and y coordinates of most of the nonhydrogen atoms were correlated by about 40%. The scale factors and some of the thermal parameters were correlated as high as 65%, but these results do not appear in the error estimation. Comparison of the final values of F_o and F_c for high intensity reflections suggested that secondary extinctions were not present to any significant extent.

Figure 2 is a drawing of a portion of Ni(n-Bu_2Dtc)$_3^+$ cation which indicates the numbering scheme along with some of the intramolecular distances and angles. In the hexagonal cell there are two such units related by a center of inversion at (00$^1/_2$). The NiS_6 core is a slightly distorted octahedron, with the Ni atoms located at (00$^1/_4$) and (00$^3/_4$) and separated by 5.384 Å.

The arrangement of atoms in the crystal is given in Figure 3. There are columns of close-packed sulfur atoms forming octahedra, with most S-S distances (Table IV) essentially related to the van der Waals radii. Nickel atoms occupy half of the octahedral interstices in each column. One notices a similarity to the nickel arsenide structure. The geometry of the two kinds of sulfur octahedra (one with and one without the nickel atom) is summarized in Table V. The bromine ions are arranged in a trigonal antiprismatic manner about these columns, fitting into pockets formed by the butyl chains. The closest Ni-Br distance is 8.306 Å. The closest contacts between bromine and the carbons in the butyl chain occur at C2 and C3 (Table IV), and the shortest nonhydrogen contact distance between butyl chains is 3.89 Å (C2 to C5'). The fact that the $S_2CN(C)_2$ group is not exactly planar (torsional angle,

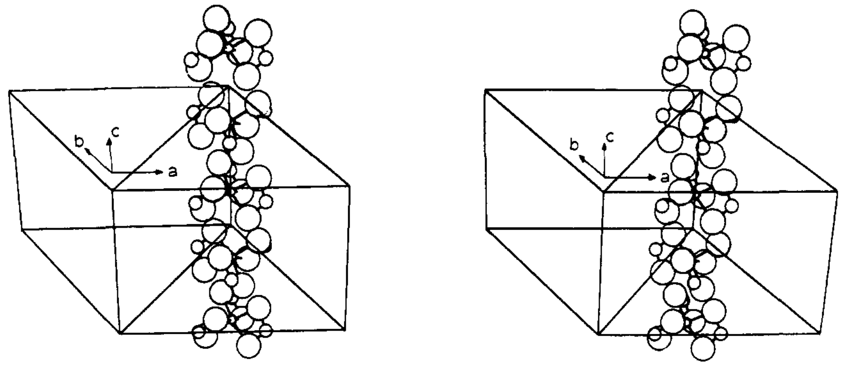

Figure 3. A stereopair packing diagram showing the columnar stacking of the Ni(n-Bu_2Dtc)$_3^+$ cation.

Table IV. Some Intermolecular Distances () for $Ni(S_2CN(C_4H_9)_2)_3Br$

S-S'[a]	2.794 (2)	Br-C4	4.038
S'-S''	3.327 (2)	Br-C3	3.861
S-S''	3.336 (2)	Br-C2	3.710
S-S'''	3.579 (2)	Br-N	4.079
S'-S'''	5.406 (2)	N-C3	2.461 (8)
Ni-Br	8.306	C2-C4	2.531 (11)
	8.898	C2-C5	3.114 (15)
Br-Br	9.898	C3-C5	2.425 (16)
Br-C5	5.289	C5-C2'[b]	3.886

[a] S and S' are in the same ligand, S'' is in the adjacent ligand on the same Ni atom, with respect to S, and S''' is bonded to the adjacent Ni atom. [b] The last distance refers to the shortest intermolecular distance between carbons in butyl chains in adjacent ligands.

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(22) A structure factor table will appear following these pages in the microfilm edition of this volume of the journal. Single copies may be obtained from the Business Operations Office, Books and Journals Division, American Chemical Society, 1155 Sixteenth St., N.W., Washington, D. C. 20036, by referring to code number JACS-73-774. Remit check or money order for $3.00 for photocopy or $2.00 for microfiche.

Table V. Comparison of $Ni(n\text{-}BuDtc)_3^+$ Octahedra in the Unit Cell Packing

Type of octahedron	Comment	Dist,[a] Å
With nickel	Twist about $\bar{3}$ of 14.64 (6)° from trigonal antiprism (32 point symmetry)	2.367
Without nickel	No twist—trigonal antiprism ($\bar{3}$ site symmetry)	3.017
Hypothetical close packing of sulfurs, assuming van der Waals radius of 1.85 Å	Octahedral (O_h)	2.62

[a] Along $\bar{3}$ between layers of sulfur atoms.

S–C1–N–C2, is 4.4°) may be indicative of a slight packing strain. The ends of the butyl chains exhibit relatively high thermal motion, but there appears to be no major disorder. The short C4–C5 bond length may be more apparent than real, as a result of vibrational effects. Judging from the values of the thermal displacements for the sulfur atoms, there appears to be no disordering. The octahedron formed by the NiS_6 core is twisted from the trigonal prismatic orientation by 45.4°.

Physical Properties of $Ni(R_2Dtc)_3X$. The infrared spectrum of $Ni(n\text{-}Bu_2Dtc)_2$ shows a "thioureide" CN stretch[23a] at 1505 cm^{-1}. This band shifts to 1545 cm^{-1} in $Ni(n\text{-}Bu_2Dtc)_3Br$. A shift from 1503 to 1514 cm^{-1} occurs upon oxidation of $Ni(Bz_2Dtc)_2$. The infrared spectra of the NO_3^- and BF_3Br^- salts of $Ni(n\text{-}Bu_2Dtc)_3Br$ showed anion frequencies at 1390 cm^{-1} (NO_3^-)[23b] and 1049 and 1065 cm^{-1} (BF_3Br^-).

The electronic spectrum of $Ni(n\text{-}Bu_2Dtc)_3Br$ has been reported by Brinkhoff.[2] Due to the sensitivity of solutions in some solvents to bleaching by heat or visible light (*vide infra*), the molar extinction coefficients are difficult to obtain accurately. Our values, Table VI, are somewhat higher than data reported (in $CHCl_3$) by Brinkhoff.

Table VI. Visible and Ultraviolet Solution Spectra of $Ni(n\text{-}Bu_2Dtc)_3Br$

Solvent	ν, kK	$10^{-3}\epsilon$, M^{-1} cm^{-1}
$CHCl_3$	18.1 (sh)	~5.6
	20.2 (sh)	~8.4
	22.8	10.3
	29.9	25.0
	37.2	44.0
CH_3CN	18.2 (sh)	~5.1
	20.2 (sh)	~7.7
	22.9	10.4

The proton magnetic resonance spectra of $Ni(n\text{-}Bu_2Dtc)_3Br$ and $Ni(Bz_2Dtc)_3Br$ in chloroform-*d* show equivalent alkyl groups. In $Ni(Bz_2Dtc)_3Br$ the benzyl protons appear as a singlet, τ 2.62, at room temperature. The τ values for methylene protons are as follows: $K(Bz_2Dtc)$ in $CDCl_3$, 4.62; DMSO-d_6, 4.57; cyclohexanone, 4.55; $(Bz_2Dtc)_2$ in CH_3CN, 4.72; $CDCl_3$, 4.73; DMSO-d_6, 4.70; cyclohexanone, 4.71; $Ni(Bz_2Dtc)_2$ in $CDCl_3$, 5.30; $Ni(Bz_2Dtc)_3Br$ in CH_3CN, 5.15; $CDCl_3$, 5.12.

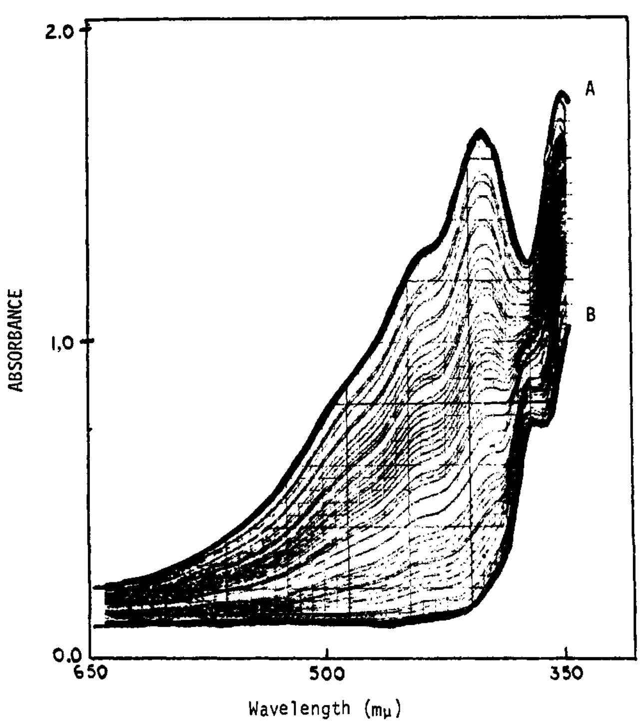

Figure 4. Spectral changes during color return for $Ni(n\text{-}Bu_2Dtc)_3Br$ in CH_3CN at 5 sec/scan: (A) before bleaching, (B) nearly total bleaching.

Conductivity measurements in CH_3NO_2 at 25° confirmed the results of Brinkhoff[2] for a 1:1 electrolyte.

The bulk magnetic susceptibility at room temperature, 21°, is $\chi^M = -2.09 \times 10^{-4}$ cgsu. With a diamagnetic correction of 4.23×10^{-4} cgsu,[24] $\mu_{eff}^{corr} = 0.7$ BM.

Photobleaching of the $Ni(R_2Dtc)_3^+$ Complexes. Solutions of the $Ni(R_2Dtc)_3^+$ complexes in nonreacting solvents are very deep red-brown in color. Treatment of any of these solutions with strong visible light results in a disappearance of the red-brown color, leaving a pale yellow solution. In some solvents a gradual return of the dark red-brown color associated with $Ni(R_2Dtc)_3^+$ occurs when the solution is allowed to stand in the dark.

The changes in the absorbance spectrum of a solution of the complex on bleaching are illustrated in Figure 4, which shows spectra obtained with a rapid scan spectrophotometer using 5-sec scans. No isosbestic point is observed in this region of the spectrum, since the absorbance of the photochemically bleached solution is less than that of the $Ni(n\text{-}Bu_2Dtc)_3Br$ solution at all wavelengths studied.

Solutions of $Ni(n\text{-}Bu_2Dtc)_3Br$ in dry acetonitrile were found to be stable for long periods of time. Repeated bleaching of the solutions with visible light over a period of months had little discernible effect upon the intensity of the color of the solutions after redarkening.

The $Ni(n\text{-}Bu_2Dtc)_3Br$ complex is soluble in a number of solvents. These can be divided into three categories on the basis of the result of treatment of the solution

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(23) (a) J. P. Fackler, Jr., and D. Coucouvanis, *Inorg. Chem.*, 6, 2047 (1967); 7, 181 (1968); (b) K. Nakamoto, "Infrared Spectra of Inorganic and Coordination Compounds," Wiley, New York, N. Y., 1963.

(24) B. N. Figgis and J. Lewis, "Modern Coordination Chemistry," J. Lewis and R. Wilkins, Ed., Interscience, New York, N. Y., 1960.

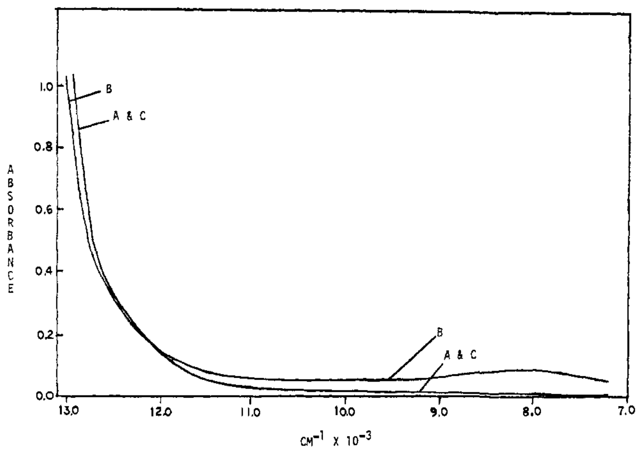

Figure 5. Near-infrared spectrum of Ni(n-Bu$_2$Dtc)$_3$Br in CH$_3$CN: (A) before bleaching, (B) after bleaching, (C) about 8 min after bleaching.

with light. In type A solvents no bleaching occurs even with dilute solutions and strong light conditions. In the solvents of type B, photochromic behavior is observed. It is also observed in mixtures of type A and B solvents, provided that the amount of type B solvent is substantial. Dilute solutions of the complex in spectral grade chloroform, for example, which contains ethanol as a stabilizer, show no photochromic behavior.

Type C solvents or solvent mixtures are ones in which the complex is photochemically bleached, but irreversibly. Solutions of the complex in these solvents lose their color in several hours even in the absence of light. The evaporation of bleached solutions of the complex in pyridine or triethylamine–chloroform regenerates the complexes.

Some solvents belonging to each of the above categories are presented in Table VII.

Table VII. Solvents of Types A, B, and C

Type A (no bleaching): CHCl$_3$, CH$_2$Cl$_2$, CHBr$_3$, CHCl$_2$CHCl$_2$, C$_6$H$_5$Br

Type B (reversible bleaching): CH$_3$CN, C$_2$H$_5$OH, CH$_3$OH, CH$_3$NO$_2$, acetone, cyclohexanone, nitrobenzene, tetrahydrofuran, isopropyl alcohol, benzyl alcohol, cyclohexanol

Type C (irreversible bleaching): pyridine, γ-picoline, triethylamine–chloroform, H$_2$SO$_4$ (98%), type B solvents with added water

Characterization of the Bleaching in Acetonitrile. Visible light causes CH$_3$CN solutions of Ni(n-Bu$_2$Dtc)$_3$Br to decrease in absorbance throughout the visible region of the spectrum. However, an increase in the absorbance is found in the near-infrared region of the spectrum and an isosbestic point can be found. The spectrum of a 2.905 × 10^{-3} M CH$_3$CN solution of Ni(n-Bu$_2$Dtc)$_3$Br in a 5-cm cell is shown in Figure 5A. The solution was treated with the photoflood lamp outside the spectrometer and the spectrum of this solution was taken as quickly as possible thereafter. This spectrum is shown in Figure 5B. After several minutes in the dark the spectrum was again taken and is shown as spectrum C. An isosbestic point is located at 815 nm (12,300 cm^{-1}). The maximum for the new band is located at 1230 nm (8100 cm^{-1}). Assuming the bleached solution contains only the species absorbing at 1230 nm, a molar extinction of ~7 M^{-1} cm^{-1} is calculated.[25] This low-energy band is readily assigned[26] to a ν_1 ($^3A_{2g} \rightarrow {}^3T_{2g}$) in "octahedral" nickel(II) to give a reasonable Dq value.

Treatment of pyridine solutions of Ni(n-Bu$_2$Dtc)$_3$Br with light gives pale green solutions from which the starting material can be recovered by evaporation of the solvent. A spectrum of Ni(n-Bu$_2$Dtc)$_3$Br in pyridine after treatment with light showed three absorbance maxima in the near-infrared and visible regions (Table VIII). The pmr spectrum of Ni(Bz$_2$Dtc)$_3$Br in CDCl$_3$ after the addition of a small quantity of pyridine followed by bleaching showed two methylene singlets at τ 4.72 and 5.28, implicating the formation of (Bz$_2$Dtc–)$_2$ and Ni(Bz$_2$Dtc)$_2$. Integration of the signals established a 2:1 ratio. Increased pyridine addition did not affect the τ 4.72 peak but caused the disappearance of the τ 5.28 resonance. Similar results were obtained with triethylamine. Photolysis in other solvents also led to the formation of (Bz$_2$Dtc–)$_2$, as did the addition of [(C$_2$H$_5$)$_2$NH$_2$] (Et$_2$Dtc).

Table VIII. Absorbance Maxima of Ni(n-Bu$_2$Dtc)$_3$Br (Bleached) in Pyridine

Max (cm^{-1})	Max (l. mol^{-1} cm^{-1})
10,100	7.3
16,100	60
20,700 (sh)	110

Kinetics of Redarkening of Photobleached Acetonitrile Solutions of Ni(n-Bu$_2$Dtc)$_3$Br. All calculations of the kinetic parameters were carried out based on methods outlined in Frost and Pearson.[27]

The rates of debleaching of the Ni(n-Bu$_2$Dtc)$_3$$^+$ cation in acetonitrile were obtained by observing the increase in absorbance at 5575 Å $vs.$ time at temperatures of 5, 15, 25, 30, 35, and 45°. Assuming ($\epsilon_T - \epsilon_B$) ≈ ϵ_T at this wavelength, where ϵ_T is the molar extinction of the unbleached material and ϵ_B the molar extinction of the bleached species, [Ni$_B$] was calculated. Plots of [Ni$_B$]$^{-1}$ $vs.$ time at the various temperatures were linear, consistent with a second-order rate law given by (1).

$$-\mathrm{d}[\mathrm{Ni_B}]/\mathrm{d}t = k_2[\mathrm{Ni_B}]^2 \qquad (1)$$

Rate constants are presented in Table IX.

The kinetics of the return of the material from the photobleached state were also examined by means of

Table IX. Second-Order Rate Constants for Return of Ni(n-Bu$_2$Dtc)$_3$Br from the Photobleached State in CH$_3$CN[a]

k_2, l. mol^{-1} sec^{-1}	Ln k_2	T,°C (±0.5°)	10^{-4}[Ni]$_0$, M
0.42 ± 0.05	−0.882	5	1.83
1.51 ± 0.1	0.412	15	1.83
5.4 ± 0.3	1.69	25	3.28
12.2 ± 0.8	2.50	30	1.73
26.5 ± 2	3.28	35	1.66
46.0 ± 3	3.83	45	1.87

[a] E_a = 21 ± 2 kcal/mol, $\Delta S^{\ddagger}$ = 14 eu.

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(25) Unfortunately this number is not accurately determined due to the rapid re-formation of the Ni(n-Bu$_2$Dtc)$_3$$^+$.

(26) C. J. Ballhausen, "Introduction to Ligand Field Theory," McGraw-Hill, New York, N. Y., 1962.

(27) A. A. Frost and R. G. Pearson, "Kinetics and Mechanism," 2nd ed, Wiley, New York, N. Y., 1961.

the change in the conductance of solutions at 25°. Photolysis of solutions of Ni(*n*-Bu_2Dtc)$_3$Br in acetonitrile or nitromethane leads to a drop of ~50% in the conductance of the solutions. In the absence of light the conductance gradually returns toward the originally measured value. A linear plot of $\Lambda_\infty - \Lambda_m$ *vs.* time, where Λ_∞ is the conductance of the unbleached solution and Λ_m is the measured conductance at any time, leads to a calculation of rate constants of 5.5 ± 0.5 M^{-1} sec^{-1} at 25°, in good agreement with the spectroscopic results.

Other Observations. The spectrum of Ni(*n*-Bu_2Dtc)$_3$Br in CH_3CN and nitrobenzene is temperature dependent with an ~20% loss in absorbance at the 4400 Å maximum occurring on raising the temperature from 25 to 55°. The data at 5575 Å are presented in Table X. At 150° in nitrobenzene the pmr spectrum of the butyl proton is very broad and poorly resolved. Lowering the temperature again to 60° sharpens the peaks.

Table X. Temperature Dependence of the Spectrum of Ni(*n*-Bu_2Dtc)$_3$Br in CH_3CN at 5575 Å

Temp, °K (±0.5°)	ε, M^{-1} cm^{-1} [a]
298	4530
303	4450
308	4310
318	4140
328	3780

[a] Values accurate to ~±40.

Qualitative observations showed that the rate of debleaching of solutions of Ni(*n*-Bu_2Dtc)$_3$Br was accelerated by the addition of thiuram disulfide. By adding (Et_2Dtc–)$_2$ to acetonitrile solutions of the complex, quantitative measurements in which the ratio of thiuram disulfide to nickel ranged from 10 to approximately 250 established a first-order dependence on disulfide concentration with an overall second-order behavior. The results are presented in Table XI.

Table XI. Rate Constants for Ni(*n*-Bu_2Dtc)$_3$Br Debleaching Obtained with Added Thiuram Disulfide

[(Et_2Dtc–)$_2$][a]	[Ni(*n*-Bu_2Dtc)$_3$Br][a]	k_2, l. mol^{-1} sec^{-1}	k_1 (sec^{-1})/[Et_2Dtc–)$_2$]
1.06×10^{-4}	2.12×10^{-4}	4.7 ± 0.5	
1.74×10^{-3}	1.73×10^{-4}	1.36 ± 0.08	
1.55×10^{-2}	1.85×10^{-4}	0.21 ± 0.02	0.21 ± 0.02
4.65×10^{-2}	1.89×10^{-4}	0.14 ± 0.01	0.14 ± 0.01

[a] In mol/l.

The addition of tetra-*n*-butylammonium bromide qualitatively strongly slows the rate in which the color associated with Ni(*n*-Bu_2Dtc)$_3$Br is reestablished after bleaching. Quantitative data were not obtained.

Phosphines also react with Ni(R_2Dtc)$_3$Br, producing Ni(R_2Dtc)R_3PBr. Ni(Et_2Dtc)P(C_6H_5)$_3$Br was prepared according to the procedure of Maxfield[28] and its physical properties compared with the products of the reaction of M(R_2Dtc)$_3$Br with phosphines. The visible spectrum of a $CHCl_3$ solution of Ni(*n*-Bu_2Dtc)$_3$Br containing triphenylphosphine closely resembles the spectrum of Ni(Et_2Dtc)P(C_6H_5)$_3$Br in this solvent.

The pmr spectrum of $CHCl_3$ solutions containing an equimolar mixture of Ni(*n*-Bu_2Dtc)$_3$Br and Ni(*n*-Bu_2Dtc)$_2$ shows only one broad α-methylene proton resonance to −90°. In 50% $CHCl_3$–toluene, a 1:1 mixture of the two complexes exhibits a three-line epr spectrum (at −140°) with *g* values of 2.212, 2.190, and 2.165.

It was found that (Et_2Dtc–)$_2$ slowly reacts with Ni(Bz_2Dtc)$_3$Br. Water reacts with Ni(R_2Dtc)$_3$Br to produce Ni(R_2Dtc)$_2$, (R_2Dtc–)$_2$, and nickel(II) bromide. Base accelerates this reaction and acid inhibits it. In the presence of light, Ni(Bz_2Dtc)$_3$Br reacts with water in isopropyl alcohol to evolve small amounts of a gas qualitatively tested to be hydrogen (flame test).

Discussion

There is little evidence in the structure of Ni(*n*-Bu_2Dtc)$_3$Br to suggest that the cation should be formulated in any way other than as nickel surrounded by three "normal" dithiocarbamate ligands. The C–S and C1–N distances of the ligand fall within the narrow 1.68–1.73- and 1.30–1.34-Å ranges found,[29] respectively, in a large number of complexes. The Ni–S distance (Table III) is similar[30] to the 2.267 Å Co–S distance reported for the isoelectronic Co(Et_2Dtc)$_3$. The interligand S···S distances (both intramolecular and intermolecular) are normal and the bromide anion is well removed from the cation center. The only structural feature somewhat atypical of dithiocarbamates generally, but also observed with the CuBr$_2$(*n*-Bz_2Dtc), is the columnar[31] stacking of the cations (Figure 3).

The physical and chemical properties of Ni(R_2Dtc)$_3$Br further corroborate the nickel(IV) formulation of the complex. The conductivity in CH_3NO_2 identifies a 1:1 electrolyte and the magnetic susceptibility, 0.71 BM at room temperature, is consistent with a $3d^6$ low-spin octahedral electronic structure for the metal ion. Reactions with bases and photochemical bleaching lead to the formation of thiuram disulfide and nickel(II) products.

The thermal bleaching of Ni(*n*-Bu_2Dtc)$_3$Br in CH_3CN, Table X, can be interpreted by assuming a disproportion equilibrium (2), assuming $^1/_2[\mathrm{Ni_B}] = [\mathrm{NiBr_2}] = [\mathrm{Ni}(n\text{-}\mathrm{Bu_2Dtc})_2] = {}^1/_2[(n\text{-}\mathrm{Bu_2Dtc}\text{–})_2]$, based on the stoichiometry of (2), and further that $[\mathrm{Br^-}] = [\mathrm{Ni}(n\text{-}\mathrm{BuDtc})_3{}^+]$ (the conductivity upon bleaching drops, suggesting that bromide is firmly coordinated to products in (2)); an equilibrium constant may be evaluated, Table XII. Further, assuming that K_T is related to the second-order rate constant k_2 (Table IX) of the debleaching process by $K_T = k_{B1}/k_2$, k_{B1} may be calculated (Table XII). Comparison of the temperature dependence of k_{B1} with k_2 suggests that $\Delta H^{\ddagger}$(bleaching) ≅ $\Delta H^{\ddagger}$(debleaching) + ΔH (equilibrium). Clearly the bleaching of Ni(Bu_2Dtc)$_3{}^+$ to nickel(II) products in CH_3CN is an "uphill" process.

$$\mathrm{Ni}(n\text{-}\mathrm{Bu_2Dtc})_3{}^+ + \mathrm{Br^-} = \frac{1}{2}\mathrm{Ni}(n\text{-}\mathrm{Bu_2Dtc})_2 + \frac{1}{2}\mathrm{NiBr_2} + (n\text{-}\mathrm{Bu_2Dtc}\text{–})_2 \quad (2)$$

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(28) P. L. Maxfield, *Inorg. Nucl. Chem. Lett.*, 6, 693 (1970).

(29) D. Coucouvanis, *Progr. Inorg. Chem.*, 11, 233 (1970).

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(31) Powder conductivity measurements, kindly made by the General Electric Co., Schenectady, N. Y., by L. Interrante, suggest no significant electrical anisotropy.

Table XII. Thermodynamic Parameters for Thermal Bleaching of Ni(n-Bu$_2$Dtc)$_3$Br in CH$_3$CN^a

T, °K	10^3K_T	k_{B1}, M^{-1} sec^{-1}
298	1.98 ± 0.07	0.011 ± 0.001
303	2.70 ± 0.08	0.033 ± 0.003
308	4.2 ± 0.1	0.11 ± 0.01
318	6.6 ± 0.2	0.30 ± 0.03
328	13.3 ± 0.4	

^{a} $\Delta H = 12 \pm 1$ kcal/mol, $\Delta S = 27 \pm 3$ eu.

A general rate expression for the debleaching of Ni(n-Bu$_2$Dtc)$_3^+$ in CH$_3$CN can be formulated (3) which

$$-\frac{d[\mathrm{Ni_B}]}{dt} = \frac{k_A[\mathrm{Ni_B}][\mathrm{L_2}]}{k_B[\mathrm{Br^-}] + k_C[\mathrm{L_2}]} \qquad (3)$$

takes into account the inhibition by Br$^-$ and (n-Bu$_2$-Dtc–)$_2$ and is consistent with the experimental expression (1) given previously and the stoichiometry of the reaction. The thiuram disulfide concentration is [L$_2$].

A reaction sequence which corresponds to this expression and is consistent with other information presented here is as follows.

$$\begin{aligned} &\mathrm{NiBr_2 + NiL_2 \xrightleftharpoons[k_{-1}]{k_1} 2NiLBr} \\ &\mathrm{NiLBr \xrightleftharpoons[k_{-2}]{k_2} NiL^+ + Br^-} \\ &\mathrm{NiL^+ + L_2 \xrightarrow{k_3} NiL_3^+} \end{aligned} \qquad (4)$$

Solvation of the various species is assumed but not indicated in these expressions. Using steady-state conditions for NiL$^+$, (5) is obtained, with $Kn = (k_1/k_{-1})^{1/2}$. This expression is seen to be consistent with (3).

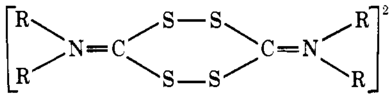
$$\frac{d[\mathrm{NiL_3^+}]}{dt} = -\frac{d[\mathrm{Ni_B}]}{dt} = \frac{Knk_2k_3[\mathrm{Ni_B}][\mathrm{L_2}]}{2(k_{-2}[\mathrm{Br^-}] + k_3[\mathrm{L_2}])} \qquad (5)$$

The NiLBr species suggested in (4) presumably could be Ni(n-Bu$_2$Dtc)(CH$_3$CN)Br, a species similar to the four-coordinate phosphine complexes isolated by Maxfield.[28]

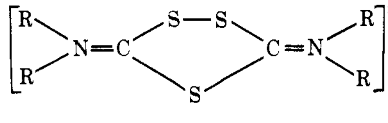
The reaction of [Ni(n-Bu$_2$Dtc)$_3$]Br with water to produce hydrogen can be rationalized if one recognizes that dithiocarbamate dications (6) may be formed.

$$\mathrm{Ni(R_2Dtc)_3^+ + Br^- + H_2O =}$$
$$\mathrm{(R_2Dtc)_2^{2+} + {}^1/_2H_2 + Ni(R_2Dtc)Br(OH)} \qquad (6)$$

These dications, II, have been suggested by others.[2]



II



III

The Nijmegen group[32] has succeeded in obtaining the crystal structure of the cation formed by iodine oxidation of the tetraethylthiuram disulfide adduct of HgI$_2$. The cation, III, has one less sulfur atom than the originally postulated formulation. We have attempted the synthesis of [(R$_2$Dtc)$_2$](FeCl$_4$)$_2$ but suitable crystals for diffraction have not been obtained.

The electron spin resonance spectrum, obtained by allowing [Ni(n-Bu$_2$Dtc)$_3$]Br to react with Ni(n-Bu$_2$Dtc)$_2$, suggests the formation of a reactive asymmetric nickel(III) intermediate of unknown stoichiometry.

Acknowledgments. Acknowledgment is made to the donors of the Petroleum Research Fund, administered by the American Chemical Society, for support of this research.

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(32) Professor Ir. J. J. Steggerda has kindly informed us of the work of P. T. Beurskens, W. P. J. H. Bosman, and J. A. Cras.