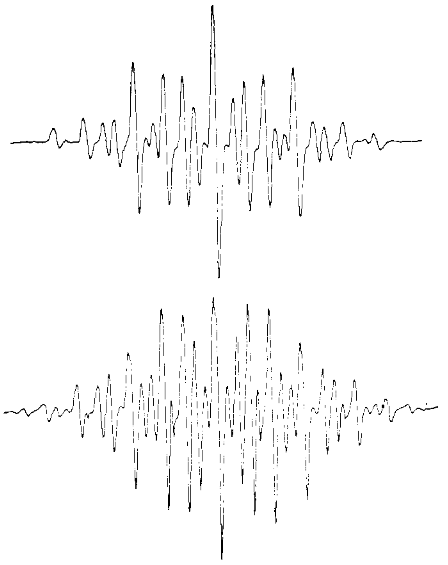

Figure 2. (Upper) The endor-induced esr spectrum of durosemiquinone from irradiation at 16.5 MHz. (Lower) The esr spectrum of durosemiquinone at −78°.

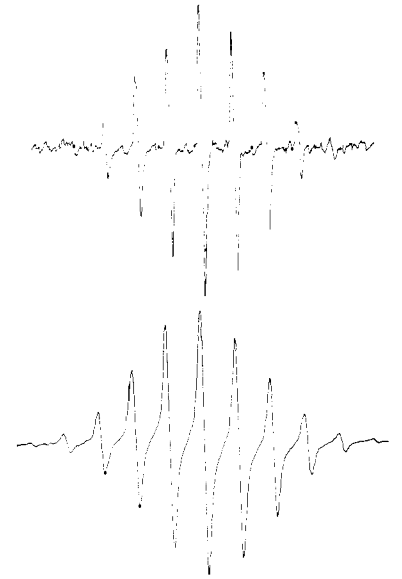

Figure 3. (Upper) The endor-induced esr spectrum of durosemiquinone from irradiation at 17.1 MHz. (Lower) The esr spectrum of durosemiquinone at +80°.

−78° by irradiating the lower frequency strong endor line at 16.5 MHz and the normal esr spectrum obtained at that temperature. Figure 3 shows the spectrum obtained under identical conditions except that the rf irradiation frequency was 17.1 MHz, that of the weak endor line. This spectrum is strikingly similar to the normal esr spectrum of the free ion or rapidly equilibrating ion pair obtained at high temperature, as can be seen from the esr spectrum taken at +80° also shown in Figure 3. Thus we believe there is a substantial amount of free ion present even at −78°. If the relative endor enhancements for the two radicals are the same, then the ratio of ion pair to free ion at −78° is about ten for a solution 10^{-3} *M* in durosemiquinone.

Another possible origin of the weak endor line is that it arises from a sodium durosemiquinone ion pair, the sodium impurity being introduced through the use of Pyrex apparatus.[6] We have prepared the radical with sodium–potassium alloy and the esr spectrum is identical with that in Figure 2, indicating that the ion-exchange equilibrium strongly favors potassium, making small amounts of sodium undetectable by esr or endor. Also, since no alkali metal splittings are observed in Figure 3, we believe our spectrum is that of the free ion. Preliminary measurements indicate that ΔH for the ion-pair dissociation reaction is negative, contrary to the previous suggestion;[2] however, the suggestion by these authors of the presence of the free durosemiquinone radical is confirmed.

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[6] P. Graceffa and T. R. Tuttle, Jr., *J. Chem. Phys.*, 50, 1908 (1969).

* Address correspondence to this author.

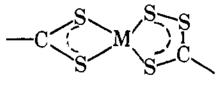
Robert D. Allendoerfer,* Richard J. Papez
Department of Chemistry, State University of New York at Buffalo
Buffalo, New York 14214

Received July 6, 1970

Structural Characterization of Tris(*N*,*N*-di-*n*-butyldithiocarbamato)nickel(IV) Bromide. A Ni–S_6 Complex with Unusual Chemical Properties

Sir:

Studies of nickel(II) dithiolates by ourselves[1,2] and others[3–5] have led to the conclusion that oxidation produces compounds which may be formulated as ligand-oxidized species. This is especially true[3] with complexes of the dithioaromatic acids[2] where oxidation has been shown to produce[6] a planar nickel(II) complex in which one of the ligands contains S_2 incorporated into a chelate ring (I). While the "extra" ligand sulfur atoms are best added by oxidation with sulfur or polysulfides, bromine or iodine oxidation of the anionic 1,1-dithiolato complexes[7] also produces sulfur-rich species, presumably by destructive oxidation of some of the ligand. Thus we were skeptical of the formulation suggested by Brinkhoff, *et al.*,[8] for the product obtained by the bromine oxidation of bis(*N*,*N*-di-*n*-butyldithiocarbamato)nickel(II), $Ni(Bu_2dtc)_2$, in CCl_4. These authors[8] described the material as tris(*N*,*N*-di-*n*-butyldithiocarbamato)nickel(IV) bromide, $Ni(Bu_2dtc)_3Br$, from their measurement of the physical and chemical properties of the material. Recently Nigo, *et al.*,[9] claimed the product of bromine oxidation of $Ni(Et_2dtc)_2$ (Et = ethyl) in $CHCl_3$ to be $Ni(Et_2dtc)_2Br_2$. Neither group apparently succeeded in producing crystallized material with a reproducible melting point.



I

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[1] J. P. Fackler, Jr., and D. Coucouvanis, *J. Amer. Chem. Soc.*, **89**, 1745 (1967).

[2] J. P. Fackler, Jr., J. A. Fetchin, and J. A. Smith, *ibid.*, **92**, 2910 (1970).

[3] G. N. Schrauzer, *Transition Metal Chem.*, 4, 229 (1968).

[4] J. McCleverty, *Progr. Inorg. Chem.*, **10**, 49 (1968).

[5] D. Coucouvanis, *ibid.*, **11**, 233 (1970).

[6] J. P. Fackler, Jr., and D. C. Fries, submitted for publication.

[7] D. Coucouvanis and J. P. Fackler, Jr., *J. Amer. Chem. Soc.*, **89**, 1346 (1967).

[8] H. C. Brinkhoff, J. A. Cras, J. J. Steggerda, and J. Willemse, *Recl. Trav. Chim. Pays-Bas*, **88**, 633 (1969).

[9] Y. Nigo, I. Masuda, and K. Shinva, *Chem. Commun.*, 476 (1970).

Following the synthetic procedure of Brinkhoff, *et al.*,[8] we obtained a material comparable to that described. Recrystallization from hot acetone followed by washing with CCl_4 and petroleum ether (30–60°) produced crystallographically suitable material[10] with mp 147–149°. While this product clearly corresponds to the material reported by Brinkhoff, *et al.*,[8] there is insufficient information in the communication by Nigo, *et al.*,[9] to be certain that they were working with a similarly formulated material, although we are led to suspect it.[11]

Inspection of Weissenberg and Buerger precession X-ray photographs of a crystal of $Ni(Bu_2dtc)_3Br$ suggest Laue symmetry $\bar{3}m$. The crystals themselves resemble hexagonal prisms. Final data collection on a Picker automatic diffractometer was conducted using a crystal roughly 0.3 × 0.6 × 0.1 mm sealed in a glass capillary. Lattice constants obtained were a = 14.386 (3) and c = 10.7677 (7) Å. From the measured density (by flotation), 1.283 (5) g/cm³, and the observed absences, $hh\bar{2h}l$, $l = 2n + 1$, the space group $D_{3d}{}^2$-$P\bar{3}1c$ (No. 163) was implicated, with two molecules per unit cell. Nickel-filtered Cu Kα radiation was used for data collection by the θ–2θ scan technique; 1349 symmetry-independent reflections ($h \geq k \geq (-2h)$, $l \geq 0$) were collected with the 5,2,0 direction chosen to be colinear to the ϕ axis to reduce the effect of multiple reflections.[12] Three independent reflections were chosen as standards and were monitored roughly every 70 reflections. A uniform 5% drop in intensity was observed during the data collection. After absorption corrections, μ = 51.05 cm^{-1} (transmission factors range from 0.28 to 0.46), and Lorentz and polarization corrections, 964 reflections were obtained which satisfied observability criteria.[13]

The structure of $Ni(Bu_2dtc)_3Br$ was solved by the heavy-atom method. Full-matrix least-squares refinement with isotropic thermal parameters led to a conventional R factor of 0.096. Introduction of modified Hughes weighting scheme and anisotropic thermal parameters produced a final converged R factor[14] of 0.052 with a weighted R, $[\Sigma w(|F_o| - |F_c|)^2]^{1/2}/\Sigma|F_o|$, of 0.065.

The molecular structure of the cation in $Ni(Bu_2dtc)_3Br$ is shown in Figure 1. The ligands are related by the threefold symmetry of the complex. The bromide anion is found at ($^1/_3$, $^2/_3$, $^1/_4$).

Crystalline $Ni(Bu_2dtc)_3Br$ dissolves to a limited extent in polar hydrocarbon solvents. It shows a conductivity typical of a 1:1 electrolyte in CH_3NO_2 (10^{-3} M). The ethyl, methyl, and benzyl analogs also have been prepared. They display properties similar to those reported by Brinkhoff, *et al.*,[8] for the butyl complex. These complexes are less stable than the butyl derivative, however, and react readily with moist air to produce $Ni(R_2dtc)_2$. When wet by acetone, $Ni(Bu_2dtc)_3Br$ also reacts with water. An acetonitrile or pyridine solution of $Ni(Bu_2dtc)_3Br$ is bleached by visible light or a toluene solution by heating. A detailed description of the chemistry of these unusual species will be reported later.

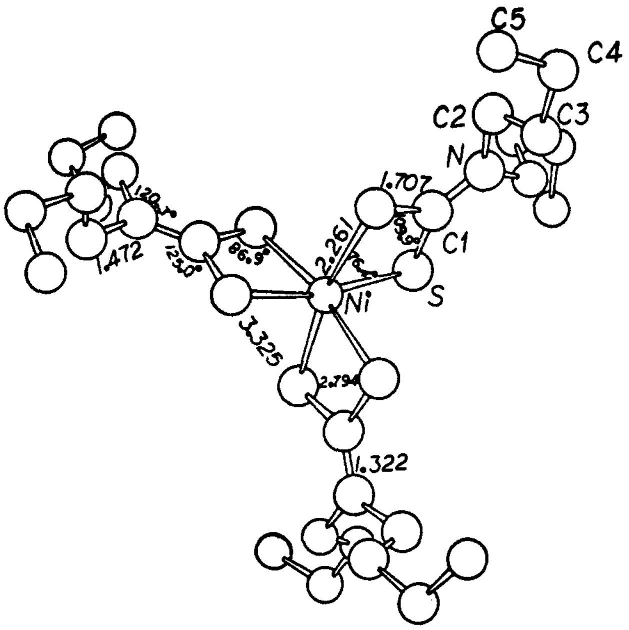

Figure 1. The structure of $Ni(Bu_2dtc)_3{}^+$ showing important distances and bond angles. Standard deviations in distances range from 0.01 to 0.06%. The Ni–Ni distance along c is 5.3838 (7) Å. The c axis has $\bar{3}$ symmetry associated with it. The equilateral triangles formed by symmetry-related intramolecular sulfur atoms are staggered by 45.36 (6)° about c. The closest intermolecular S···S contact is 3.579 (2) Å.

Structurally the coordination geometry in $Ni(Bu_2dtc)_3{}^+$ is similar to the tris(xanthato)nickelate(II) anion in[15] $[(CH_3)_3NC_6H_5]Ni(S_2COC_2H_5)_3$, a high-spin complex of nickel(II).[16] The longer mean Ni–S bond length of about 2.41 Å in the anion is consistent with the reduced formal positive charge on the metal compared with the dithiocarbamate cation. The Ni–S distance in $Ni(Bu_2dtc)_3Br$ is equally consistent with the description of the metal ion as nickel(IV). However, considering the oxidizing capabilities estimated for nickel(IV) species[17] and the ease with which dithiocarbamates are oxidized to thiuram disulfides[18] (eq 1) (II), it is naive to describe the nickel ion in $Ni(R_2dtc)_3{}^+$ as containing ionic nickel(IV), although such a description is convenient in naming the material. As nickel(IV) it would be isoelectronic with the well-established $Co(R_2dtc)_3$ complexes[5] and perhaps also isoelectronic with the interesting[19] $Fe(Et_2dtc)_2(S_2C_2(CF_3)_2)$, although this latter compound contains a 1,2-dithiete ligand known to induce unusual electronic effects.

$$2R_2NCS_2{}^- \longrightarrow R_2NC(S)S\text{–}SC(S)NR_2 + 2e^- \qquad (1)$$

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[10] *Anal.* Calcd for $NiS_6C_{27}N_3H_{54}Br$: C, 43.14; H, 7.24; S, 25.6; Br, 10.7; Ni, 7.48. Found (Galbraith and Crobaugh Laboratories): C, 43.35; H, 7.27; S, 25.8; Br, 10.8; Ni, 7.49.

[11] The infrared and visible spectral data of Nigo, *et al.*,[9] as well as the nmr spectrum, are comparable to the data we have obtained for $Ni(Et_2dtc)_3Br$ and $Ni(Bu_2dtc)_3Br$.

[12] W. H. Zachariasen, *Acta Crystallogr.*, **18**, 705 (1965).

[13] G. H. Stout and L. H. Jensen, "X-Ray Structure Determination," Macmillan, New York, N. Y., 1968, p 454 ff; $\sigma_{I_{rel}} = [\sigma_{PK}{}^2 + (0.02 \cdot N_{PK})^2]^{1/2}$.

[14] Standard crystallographic programs modified for the UNIVAC 1108 were kindly supplied by Dr. David C. Fries, whose help in their use is greatly appreciated.

[15] A. D'Addario, D. Holah, and K. Knox, private communication.

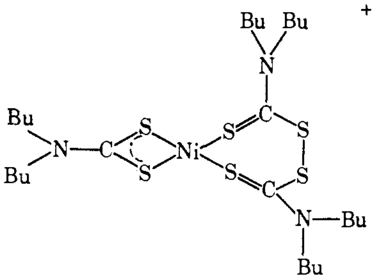
[16] D. Coucouvanis and J. P. Fackler, Jr., *Inorg. Chem.*, **6**, 2047 (1967).

[17] W. M. Latimer, "Oxidation Potentials," 2nd ed, Prentice-Hall, Englewood Cliffs, N. J., p 202.

[18] Iodine or $I_3{}^-$ and even $Fe(CN)_6{}^{3-}$ easily accomplish this oxidation: G. D. Thorn and R. A. Ludwig, "The Dithiocarbamates and Related Compounds," Elsevier, New York, N. Y., 1962, p 61.

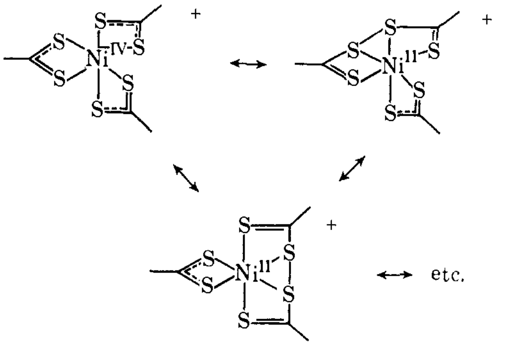
[19] L. H. Pignolet and R. H. Holm, *J. Amer. Chem. Soc.*, **92**, 179 (1970).

Since transition metal complexes of thiuram disulfide, $[R_2NC(S)S]_2$, have been prepared,[20] it appeared reasonable, in the absence of X-ray structural data, to formulate $Ni(Bu_2dtc)_3^+$ as a planar cationic complex (II) of nickel(II). Indeed thiuram disulfide can be used to prepare compounds having visible and infrared spectra identical with that of the corresponding $Ni(R_2dtc)_3Br$. On addition of the disulfide to a solution of $Ni(Bu_2dtc)_3Br$ photochemical and thermal bleaching is inhibited. The return of the brown color associated with $Ni(Bu_2dtc)_3^+$ is accelerated by adding the disulfide to the bleached solutions. We tentatively ascribe the bleaching to a reduction of the metal to nickel(II) and formation of thiuram disulfide.



II

Recognizing the unequivocal evidence that the nickel in $Ni(Bu_2dtc)_3Br$ is surrounded symmetrically by three formally uninegative dithiocarbamate ligands, the cation clearly is electron deficient relative to normal oxidation states for the elements involved. In looking for reasons for the apparent stability of the cation, it seems plausible that oxidation involving the ligands is important. In a valence-bond description, this may be depicted by resonance structures such as those in eq 2.[21]


(2)

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(20) G. Contreras and H. Cortes, *Inorg. Nucl. Chem. Lett.*, **6**, 225 (1970).

(21) We acknowledge support from the National Institutes of Health, Grant No. AM-13558-02, and the National Science Foundation, Grant No. GP-11701, for this study.

* Address correspondence to this author.

A. Avdeef, J. P. Fackler, Jr.,* R. G. Fischer, Jr.
Department of Chemistry, Case Western Reserve University
Cleveland, Ohio 44106

Received July 13, 1970

Photochemistry of Di-*tert*-butyl Ketone and Structural Effects on the Rate and Efficiency of Intersystem Crossing of Aliphatic Ketones

Sir:

The current communication deals with photochemistry and fluorescence studies of di-*tert*-butyl ketone and their implication on the rate of intersystem crossing of aliphatic ketones.

Photolysis of di-*tert*-butyl ketone (5 g) in pentane (100 ml) with a 200-W Hanovia medium-pressure Hg arc yielded three major organic products, isobutane, isobutylene, and 2,2,3,3-tetramethylbutane, and three minor products, the sum of which accounted for less than 1% of total products.[1] A sizable amount of gas was evolved durng the irradiation (identified as CO by glc on a molecular sieve 5A column). The yield of CO was 90% on the basis of ketone decomposed.

$$(CH_3)_3CCOC(CH_3)_3 \xrightarrow{h\nu} (CH_3)_3CH + (CH_3)_2C{=}CH_2 + (CH_3)_3CC(CH_3)_3 + CO$$

Kinetic analyses were carried out in hexane solution (0.576 *M*) at 3130 Å with an apparatus previously described.[2] The disappearance of starting ketone follows zero-order kinetics up to 40% conversion. The quantum yield of ketone decomposition using a ferrioxalate actinometer and pinacolone as a secondary standard[3] was found to be 0.71 ± 0.04. Similarly, the quantum yields of CO and 2,2,3,3-tetramethylbutane formation were 0.62 ± 0.03 and 0.10 ± 0.01, respectively. The relative quantum yields of the ketone decomposition in the presence of varying concentration of *cis*-piperylene were determined. The Stern–Volmer plot (Figure 1), as in the case of other *tert*-butyl ketones,[3] is nonlinear. The plot was analyzed as a composite from two linear plots derived from two reactive states, a more readily quenchable state with a slope of 1.10 M^{-1} and a less readily quenchable state with a slope of 0.08 M^{-1}. The quantum yield for ketone decomposition *via* the singlet excited state (ϕ_s) was determined to be 0.31 from the intercept by extrapolating the linear plot of the less readily quenchable state to zero quencher concentration,[4] while the quantum yield for ketone decomposition *via* the triplet state (ϕ_t) was obtained as the difference between ϕ and ϕ_s to be 0.40.

The lifetime of the singlet excited state of di-*tert*-butyl ketone was determined by a double-quenching experiment using biacetyl as the singlet energy acceptor. The quenchers used were mixtures of biacetyl and *cis*-piperylene. The total quencher concentration was maintained at 3 *M*, while the concentration of biacetyl was varied from 0.025 to 0.15 *M*. A linear Stern–Volmer plot was obtained by plotting ϕ_0/ϕ against the biacetyl concentration with a slope of 44.5 l. mol^{-1}. Assuming either quencher has equal efficiency as a triplet-state quencher, any quenching with varying concentration of biacetyl will be due to the energy transfer from the singlet excited state of di-*tert*-butyl ketone to biacetyl. Assuming the rate of energy transfer in hexane is 1×10^{10} l. mol^{-1} sec^{-1}, the lifetime of singlet excited state of di-*tert*-butyl ketone is estimated at 4.45 nsec. In a separate experiment of the lifetime of singlet excited state was determined from the fluorescence of di-*tert*-butyl ketone by the single-photon counting technique[5] to 5.6 ± 0.5 nsec. The lifetimes

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(1) The vapor-phase photolysis of di-*tert*-butyl ketone at elevated temperature has been reported by J. W. Kraus and J. G. Calvert, *J. Amer. Chem. Soc.*, **79**, 5921 (1957).

(2) D. R. Coulson and N. C. Yang, *ibid.*, **88**, 4511 (1966).

(3) N. C. Yang and E. D. Feit, *ibid.*, **90**, 504 (1968).

(4) F. S. Wettack, G. D. Renkes, M. G. Rockley, N. J. Turro, and J. C. Dalton, *ibid.*, **92**, 1794 (1970).