solution, 4:1 by volume. N.m.r. spectra indicate that the bronze product is the pure *trans* isomer; yield 0.39 g., 17%.

cis-**Bis(acetylacetonato)diamminecobalt(III) Iodide.**—The filtrates from the extractions of fractions 1 and 2 in the preceding section containing primarily the *cis*-diammine isomer were combined and evaporated to dryness, giving about 0.75 g. of crude product.

The crude *cis* crystals were extracted again in the same manner as in the previous section using about 120 ml. of an ethanol–ether solution, 4:1 by volume. The solution was filtered and evaporated to dryness.

The crystals remaining after evaporation were extracted a third time. This time the crystals were extracted with about 50 ml. of an ethanol–water–ether solution, 4:1:1 by volume, and filtered. The filtrate was evaporated to about one-half volume and refiltered. The crystals recovered were washed with two 4-ml. portions of a cold ethanol–ether solution, 1:1 by volume. N.m.r. spectra showed this to be the pure *cis* product; yield 0.08 g., 3.4%.

Chloroform extractions of the *cis* isomer were used as an alternative procedure for the separation of the *cis* and *trans* isomers. The chloroform evaporated faster, a definite advantage.

trans-**Bis(acetylacetonato)diamminecobalt(III) Chloride.**—Silver chloride was made by dissolving 0.20 g. of silver nitrate (1.2 mmoles) in 10 ml. of water and adding an excess of concentrated sodium chloride solution. The silver chloride was filtered and washed with 10 ml. of water and 5 ml. of ethanol. Then 0.39 g. of *trans*-$[Co(acac)_2(NH_3)_2]I$ (0.93 mmole) was ground with the freshly precipitated silver chloride in 15–20 ml. of an ethanol–water solution, 4:1 by volume. After filtration the silver iodide was washed with two 5-ml. portions of the ethanol–water solution. The combined filtrates were evaporated to dryness. The bronze crystals were recrystallized by dissolution in about 15 ml. of warm ethanol (*ca.* 55°) and filtration of the warm solution. Then 15 ml. of ether was added to the filtrate and the mixture was allowed to cool. The solution was filtered and the precipitate was washed with two 5-ml. portions of an ethanol–ether solution, 1:1 by volume; yield 0.18 g., 60%.

cis-**Bis(acetylacetonato)diamminecobalt(III) Chloride.**—Silver nitrate (0.16 g., 0.96 mmole) was dissolved in 10 ml. of water. Silver chloride was precipitated by adding an excess of a concentrated aqueous sodium chloride solution. The solution was filtered, and the precipitated silver chloride was washed with 10 ml. of water and 5 ml. of ethanol.

The freshly precipitated silver chloride was ground thoroughly with 0.31 g. of *cis*-bis(acetylacetonato)diamminecobalt(III) iodide (0.71 mmole) in 15 ml. of ethanol. After filtration, the silver iodide was washed with two 5-ml. portions of ethanol. The combined filtrate and washings were evaporated to dryness.

The violet crystals were recrystallized by dissolving them in about 10–15 ml. of ethanol. The solution was allowed to evaporate to about one-half its volume. The solution was cooled and filtered. The crystals were washed with two 1-ml. portions of cold ethanol; yield 0.16 g., 66%.

Infrared Spectra.—All infrared spectra were obtained on a Beckman Model IR-5A infrared spectrophotometer. Potassium bromide pellets of the complexes were prepared and used for obtaining the spectra.

Visible–Ultraviolet Spectra.—The visible and ultraviolet spectra of all of the complexes were obtained with a Cary Model 14 recording spectrophotometer or a Beckman Model DB recording spectrophotometer using aqueous or methanolic solutions in 1-cm. cells.

Proton N.m.r. Spectra.—All proton n.m.r. spectra were obtained on a Varian Model A-60 high-resolution spectrometer at 60 Mc. using tetramethylsilane as an internal standard whenever possible. The D_2O spectra are relative to a tetramethylsilane external standard (TMS–$CHCl_3$–CCl_4 solution, 1:5:5 by volume).

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N,N'-Dicyclohexylthiourea and N,N'-Diphenylthiourea Complexes of Cobalt(II)

BY G. YAGUPSKY AND R. LEVITUS

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The N,N'-dicyclohexylthiourea (DCTU) and N,N'-diphenylthiourea (DPTU) complexes of Co(II) have been investigated. In organic solvents four-coordinated tetrahedral (or pseudo-tetrahedral) species are formed. Evidence is presented to indicate that both ligands undergo a structural change in solution (postulated to be a *cis–trans* isomerism) which affects their coordinating tendencies. The solid complexes $[Co(DCTU)_6]X_2$ (X = NO_3, ClO_4) involve octahedrally-coordinated Co(II), providing the first examples of six-coordinated Co(II) complexes containing solely unidentate sulfur ligands. The factors governing the coordination number of the complexes, both in solid state and in solution, are discussed.

Introduction

Cotton, *et al.*,[1] have recently reported the syntheses and physical properties of a series of compounds involving thiourea (TU) coordinated to the Co(II) ion. They found that the complexes are tetrahedral, except $Co(TU)_4(NO_3)_2$, which is probably octahedral. From the analyses of their electronic spectra, it was inferred that thiourea occupies a position comparable to various oxygen ligands in the spectrochemical series and that it

(1) F. A. Cotton, O. D. Faut, and J. T. Mague, *Inorg. Chem.*, **3**, 17 (1964).

causes a remarkably large nephelauxetic effect. Similar results were reported by Holt and Carlin[2] for the ethylenethiourea–Co(II) complexes. Further, Yagupsky, *et al.*,[3] have prepared several tetrahedral and octahedral compounds of general formula $Co(NCS)_2 \cdot 2L$ (L = thiourea or substituted thiourea) and discussed the factors governing the stereochemical arrangement around the Co(II) ion.

The present investigation has been undertaken in order to gain additional information on the roles of charge distribution in the metal–ligand bond and of intramolecular steric effects in determining the coordination number of the Co(II) ion in complexes containing substituted thioureas.

Results

N,N-Dicyclohexylthiourea (DCTU) Complexes.— The compounds $[Co(DCTU)_6]X_2$ ($X = NO_3, ClO_4$) can be easily prepared by the interaction between an excess of DCTU and the appropriate Co(II) salt in ethyl alcohol. They are light brown crystalline solids, soluble in certain organic liquids, and nonhygroscopic. The infrared spectra of the solids indicate that anions are in the ionic form.[4,5] Further, the magnitudes of the magnetic moments (*ca.* 4.9 B.M. at 20°) are clearly indicative of octahedral Co(II).[6]

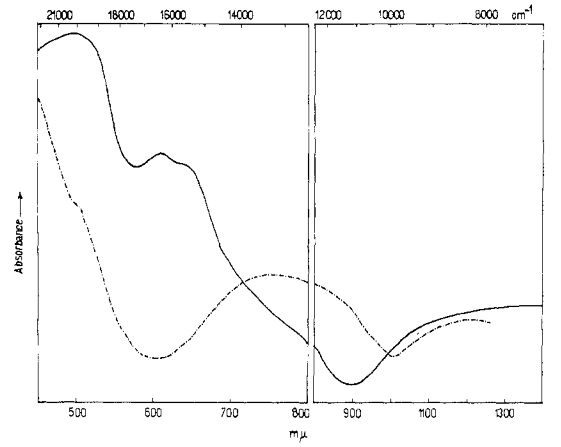

Figure 1.—Spectra of solids: full line, $[Co(DCTU)_6](NO_3)_2$; Dot–dash line, $[Ni(DCTU)_6](NO_3)_2$.

Table I

Magnetic and Spectral Data of the Co(II) and Ni(II) Complexes with DCTU

State	Magnetic moments, B.M. (20°)	Spectral data ν_{max}, cm.$^{-1}$ (ϵ) Visible	Near-infrared
$[Co(DCTU)_6](ClO_4)_2$			
Powdered solid	4.90	16,670 16,120	7500
Acetone, 10^{-3} *M* + DCTU ($DCTU:Co^{+2}$ = 25:1)		15,630 (160) sh 14,350 (240) 13,600 (220)	
Acetone, 10^{-3} *M* + DCTU ($DCTU:Co^{+2}$ = 50:1)		15,630 (390) sh 14,350 (620) 13,600 (570)	7200 (100)
Acetone, mother liquors after ppn. of $[Co(DCTU)_6](ClO_4)_2$[a]		15,625 (320) sh 14,490 (410) 13,700 (310)	
DMF, 5 × 10^{-3} *M* + DCTU ($DCTU:Co^{+2}$ = 10:1)		24,690 (18) 20,830 (12.5) 19,050 (17) 15,400 (2.5)	
DMF, 5 × 10^{-3} *M* + DCTU ($DCTU:Co^{+2}$ = 50:1)		24,690 (73) 20,000 (25,5) 15,400 (8.5)	
DMF, 5 × 10^{-3} *M* + DCTU ($DCTU:Co^{+2}$ = 90:1)		24,690 (160) 20,000 (36) 15,400 (15)	
$[Co(DCTU)_6](NO_3)_2$			
Powdered solid	4.90	16,390 15,630	7500
Acetone, 5 × 10^{-3} *M*		17,860 18,970 sh	
Acetone, 5 × 10^{-3} *M* + DCTU		15,630 14,820 13,890	
$[Co(DCTU)_3Cl_2]$			
Powdered solid		15,400 14,290	
$[Co(DCTU)_2(NCS)_2]$			
Powdered solid	4.55	15,870 14,800	7260
$[Ni(DCTU)_6](ClO_4)_2$			
Powdered solid	3.20	20,000 sh 12,500–13,500	8000–8500

[a] Only the relative values of the molar extinction coefficients are meaningful.

Since the electronic spectra of solutions are highly dependent upon the nature of the solvent and the concentration of solute (*vide infra*), we take the spectra of the solids as the true electronic spectra of the complexes. These spectra do not, of course, afford any information on band intensities. The visible spectrum of $[Co(DCTU)_6](NO_3)_2$—which is virtually identical with that of the perchlorate salt—is shown in Figure 1. Two main absorption bands are observed at *ca.* 7500 and 16,000–16,500 cm.$^{-1}$ (Table I). In addition there is a strong band, presumably due to a charge-transfer transition, at *ca.* 20,000 cm.$^{-1}$. The selection of absorption maxima for the broad bands is necessarily somewhat arbitrary and has been done by visual estimation of the center of gravity of the total intensity. Further, we shall assume, for the purpose of assignment, that the complexes have point symmetry O_h. Following Ballhausen,[7] the band in the near-infrared corresponds with the $\nu_1(^4T_1(F) \rightarrow {}^4T_2(F))$ transition. From this energy, ignoring the $^4T_1(F) \rightarrow {}^4T_1(P)$ interaction, we obtain Δ_0 = 9400 cm.$^{-1}$. Consequently, the ν_2 band ($^4T_1(F) \rightarrow {}^4A_2(F)$) should occur at around 17,000 cm.$^{-1}$. In this region the spectrum has only a broad band which tails to lower energies. As it has been frequently observed in octahedral Co(II) complexes that the ν_3 band ($^4T_1(D) \rightarrow {}^4T_1(P)$) is stronger than the ν_2 band,[7] it seems likely that both transitions contribute to the absorption in the range 15,000–17,000 cm.$^{-1}$. Using these energies, we can solve in each case for the parameter B'. The values of B' fall in the range 500–640 cm.$^{-1}$, as expected for a large nephelauxetic effect.

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(2) R. L. Carlin and S. L. Holt, Jr., *Inorg. Chem.*, **2**, 849 (1963).

(3) G. Yagupsky, R. Negrotti, and R. Levitus, *J. Inorg. Nucl. Chem.*, in press.

(4) B. M. Gatehouse, S. E. Livingstone, and R. S. Nyholm, *J. Chem. Soc.*, 4222 (1957).

(5) B. J. Hathaway and A. E. Underhill, *ibid.*, 3091 (1961).

(6) B. N. Figgis and R. S. Nyholm, *ibid.*, 12 (1956).

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

Regarding the magnitude of Δ_0, it is somewhat lower than the reported value (10,700 cm.$^{-1}$)[1] for the average field in $Co(TU)_4(NO_3)_2$, and, on the other hand, it is very close to that of the aquo group in $[Co(H_2O)_6]^{+2}$ (9300 cm.$^{-1}$).

In order to test our results, the Ni(II) complexes, $[Ni(DCTU)_6]X_2$ ($X = NO_3$, ClO_4) were prepared. These are yellow crystalline solids, isostructural with the Co(II) analogs. Their magnetic moments (*ca.* 3.2 B.M. at 20°) are typical of octahedral Ni(II). The spectrum of solid $[Ni(DCTU)_6](NO_3)_2$ (Figure 1) has bands at *ca.* 8000–8500, 12,500–13,500, and 20,000 cm.$^{-1}$. The latter band appears as a shoulder on the charge-transfer band. These bands can be assigned, respectively, to the ν_1 ($^3A_2 \rightarrow {}^3T_2(F)$), ν_2 ($^3A_2 \rightarrow {}^3T_1(F)$), and ν_3 ($^3A_2 \rightarrow {}^3T_1(P)$) transitions. Assuming $\nu_1 = \Delta_0$, and solving the approximate equation $B' = (\nu_2 + \nu_3 - 3\Delta_0)/15$,[8] we obtain the ligand field parameters, $\Delta_0 = 8000\text{–}8500$ cm.$^{-1}$ and $B' = 550\text{–}630$ cm.$^{-1}$. In excellent agreement with the results for the Co(II) analog, Δ_0 is quite similar to that in $[Ni(H_2O)_6]^{+2}$ (8500 cm.$^{-1}$), while B' is decreased very considerably from the free ion value.

The data presented in Table I indicate that the behavior of the complexes $[Co(DCTU)_6]X_2$ ($X = NO_3$, ClO_4) in acetone is dependent upon the coordinating tendencies of the respective anions. Accordingly, each derivative will be discussed separately.

$[Co(DCTU)_6](ClO_4)_2$ dissolves in acetone to give a pale pink solution, which has a visible spectrum virtually identical with that of cobalt(II) perchlorate in the same conditions. This suggests that the complex interacts with acetone to yield the octahedral ion $[Co(acetone)_6]^{+2}$ as the main species in solution. Successive additions of small amounts of DCTU cause a progressive change in the color of the solution, which turns blue, evidently due to conversion of octahedral to tetrahedral species. When the Co(II) : DCTU ratio reaches the value 1 : 50, the spectrum of the tetrahedral species is very similar to those of the complexes $[CoL_4](ClO_4)_2$ (L = thiourea or substituted thiourea)[1,2] (Figure 2, Table I). Since further addition of DCTU does not alter appreciably the spectrum of the blue solution, it can be concluded that the spectrum of an acetone solution of $[Co(DCTU)_6](ClO_4)_2$ containing a large excess of DCTU is largely, if not entirely, that of the tetrahedral ion $[Co(DCTU)_4]^{+2}$. This solution is unstable upon standing, leading to slow separation of solid $[Co(DCTU)_6](ClO_4)_2$. After precipitation has ceased, which takes several days, the mother liquor remains blue, but its visible spectrum has distinctive features which distinguish it from that of the initial solution (Figure 2). This spectrum will be discussed more fully below in connection with the N,N′-diphenylthiourea complexes.

The nitrate salt, on the other hand, dissolves in acetone to give a violet solution. Its visible spectrum (Table I, Figure 2) is very similar to that of the complex anion $[Co(O_2NO)_4]^{-2}$, suggesting considerable rearrangement of the solute.[9] As additional DCTU is added to the solution, the absorption due to the tetranitrato ion is lowered, while new bands appear in the 13,500–16,500 cm.$^{-1}$ region (Table I). The visible spectrum of the solution containing a large excess of DCTU parallels that of the blue tetrahedral species $[Co(DCTU)_4]^{+2}$ discussed above (Figure 2). Further, the behavior of the blue solution upon standing is similar to that shown by the perchlorate salt.

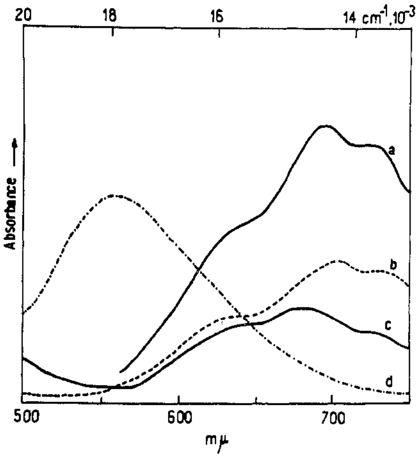

Figure 2.—Solution spectra in acetone: a, $[Co(SCN_2H_4)_4]^{+2}$ ($Co(ClO_4)_2 \cdot 6H_2O$ + large excess of thiourea); b, $Co(ClO_4)_2 \cdot 6H_2O$ + large excess of DCTU; c, mother liquors after precipitation of $[Co(DCTU)_6](ClO_4)_2$; d, $[Co(DCTU)_6](NO_3)_2$. Ordinates are different for each curve.

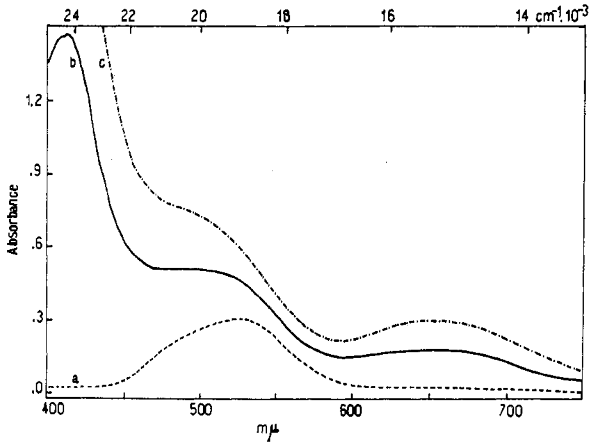

Figure 3.—Solution spectra in DMF of $Co(ClO_4)_2 \cdot 6H_2O$ + DCTU: a, $Co(ClO_4)_2 \cdot 6H_2O$ (5×10^{-3} *M*); b, a + DCTU (250×10^{-3} *M*); c, a + DCTU (450×10^{-3} *M*).

The nitrate and perchlorate salts interact with N,N-dimethylformamide (DMF) to yield the octahedral species $[Co(DMF)_6]^{+2}$.[10] On addition of increasing amounts of DCTU the spectrum shows a new band at about 15,000 cm.$^{-1}$, together with a strong charge-transfer band at about 20,000 cm.$^{-1}$ (Figure 3). The band at about 15,000 cm.$^{-1}$ is intimately related with that located in the same position in the spectrum of a saturated solution of $[Co(DCTU)_6](ClO_4)_2$ (see below).

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[8] Y. Tanabe and S. Sugano, *J. Phys. Soc. Japan*, **9**, 753 (1954).

[9] D. K. Straub, R. S. Drago, and J. T. Donoghue, *Inorg. Chem.*, **1**, 848 (1962); F. A. Cotton and T. C. Dunne, *J. Am. Chem. Soc.*, **84**, 2013 (1962); J. C. Bergman and F. A. Cotton, *ibid.*, **86**, 2491 (1964).

[10] S. Buffagni and T. M. Dunn, *J. Chem. Soc.*, 5105 (1961).

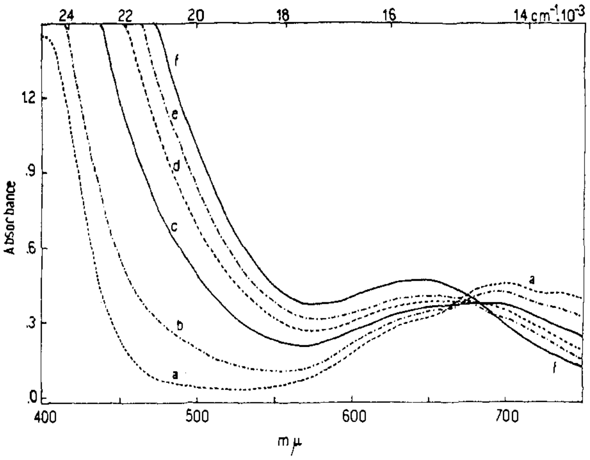

Figure 4.—Spectra in acetone of $Co(ClO_4)_2 \cdot 6H_2O$ (0.93×10^{-3} *M*) + excess DPTU: a, initial solution; b, 2 hr.; c, 5 hr.; d, 7 hr.; e, 9 hr.; f, 48 hr.

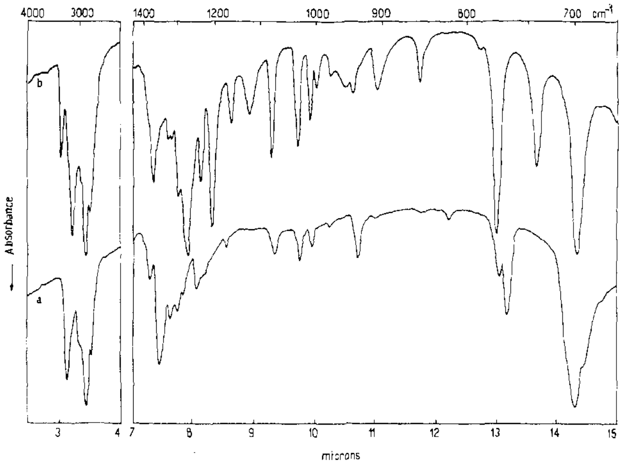

Figure 5.—Infrared spectra (Nujol mulls): a, N,N′-diphenylthiourea, stable form; b, N,N′-diphenylthiourea, unstable form.

N,N′-Diphenylthiourea (DPTU) Complexes.—Attempts to prepare pure solid DPTU complexes of Co(II) were unsuccessful (see Experimental section). Consequently, the investigation of the coordinating properties of this ligand toward the Co(II) ion was limited to spectral and conductivity measurements in solution.

Successive additions of small amounts of DPTU to cobalt(II) perchlorate in acetone changes the typical spectrum of $[Co(acetone)_6]^{+2}$ to that of the blue tetrahedral species $[Co(DPTU)_4]^{+2}$, as inferred from the position of the new bands and their respective intensities. It is assumed that the Co(II) ion is completely converted to the species $[Co(DPTU)_4]^{+2}$ when further addition of free ligand does not cause significant variation in the spectrum of the blue solution. The color of the solution changes slowly, upon standing, from blue to green and finally brown. The various stages of this transformation can be followed by concomitant changes in the visible spectrum of the involved species (Figure 4). The absorption of the blue solution in the 13,500–16,500 cm.$^{-1}$ region gradually disappears and is replaced by a new band at about 15,000 cm.$^{-1}$, together with a strong charge-transfer band at about 24,000 cm.$^{-1}$ (which gives the brownish color to the solution). The extinction coefficient of the 15,000 cm.$^{-1}$ band was estimated by assuming a maximum contribution from the charge-transfer band of 30%, as estimated by inspection. This gives ϵ 300 and a band width of about 2500 cm.$^{-1}$.

In passing from the initial to final species, various successive isosbestic points can be detected in the visible region (Figure 4), namely at 15,151, 14,550, and 14,490 cm.$^{-1}$. Regarding the features of the spectra in the near-infrared, the initial blue solution in acetone containing a large excess of DPTU shows a band at *ca.* 7500 cm.$^{-1}$, characteristic of the tetrakis-thiourea (or substituted thiourea) complexes listed in Table I. This band disappears on standing and the brownish final solution does not show any absorption in this region. Further, the final solution has a band at about 4500 cm.$^{-1}$ in the low end of the near-infrared. Unfortunately, measurements in this region are not very reliable because of the simultaneous presence of vibrational overtone and combination bands of the ligand.

On the other hand, the conductivity of the acetone solution during the transformations remains practically constant. The molar conductance of a 0.5×10^{-3} *M* solution, 190–195 ohm^{-1} mole^{-1} cm.$^{-2}$, indicates that the involved species are correctly viewed as 1:2 electrolytes.[2]

Since the transformation from the blue to the brownish solution is very slow as compared with normal ligand exchange reactions of Co(II) complexes, we infer that it is caused by a kinetically slow structural change in the ligand which affects its coordinating tendencies. This is substantiated by the fact that aged solutions of DPTU in acetone afford a brown solution instantaneously on addition of cobalt(II) perchlorate. The transformation also occurs in the absence of light and in a system rigorously protected from air, thus ruling out the possibility of both a photochemical and oxidation reaction. Moreover, very slow evaporation of aged solutions of DPTU in acetone yields a different crystalline form of the ligand, which gradually reverts to the original, apparently more stable, form. The infrared spectra of both forms of DPTU are shown in Figure 5. It can be noted that the spectrum of the transformed substance is more complex, having more bands than that of the original form. The most significant differences are found in the C–H out-of-plane wag (700–800 cm.$^{-1}$) and N–H stretching (3000–3400 cm.$^{-1}$) regions. This would suggest that the transformed molecule has a lower effective symmetry than the original form. At the same time, the ultraviolet spectra of both forms are virtually identical, showing a $n \rightarrow \pi^*$ band at 316 mμ, which indicates that the transformation does not involve a fundamental change in the nature of the chemical bonds.

The available evidence suggests the occurrence of geometrical isomerism. Examination of molecular models shows that, assuming N–C–S conjugation, two

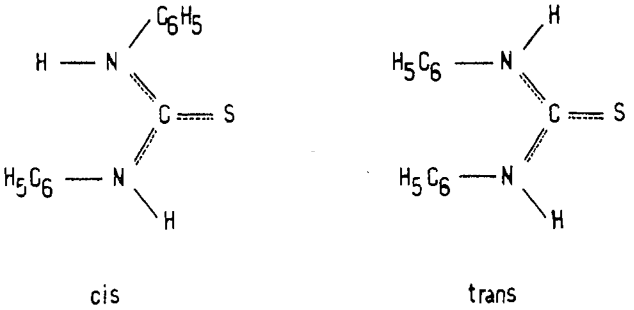

Figure 6.

geometrical arrangements are, in principle, possible for the phenyl groups as shown in Figure 6. It can be seen that in the *trans* form the phenyl groups are equivalent, while the *cis* form has, apparently, no symmetry at all. Therefore, we tentatively conclude that the stable DPTU molecule has the *trans* configuration whereas the transformed ligand has the *cis* arrangement. As an aside, it may be noted that the rate of transformation is dependent on the nature of the solvent. Thus, addition of an excess of DPTU to cobalt(II) perchlorate in DMF yields directly the brown species, while the same reaction in methylene chloride yields a blue solution, which remains unaltered for long periods.

Discussion

The blue solution obtained by addition of a large excess of DPTU to cobalt(II) perchlorate in acetone is, as stated before, virtually identical with those of the tetrahedral tetrakis cations listed in Table I. Hence, the ligand field parameters Δ_t = 4250 and B' = 600 cm.$^{-1}$ are assigned to DPTU in the blue species [Co(DPTU)$_4$]$^{+2}$ (see Table II). On the other hand, the spectrum of the brownish transformed solution is rather peculiar since it lacks a band in the 5000–7000 cm.$^{-1}$ region. Nevertheless, the intensity of the band in the visible and its oscillator strength (Table II) are characteristic of tetrahedral (or pseudo-tetrahedral) Co(II). On the assumption that this is the ν_3 transition ($^4A_2(F) \rightarrow {}^4T_1(P)$), then the remaining band at *ca.* 4500 cm.$^{-1}$ in the near-infrared can be assigned to the ν_2 ($^4A_2(F) \rightarrow {}^4T_1(F)$) transition. From these energies and using the appropriate equations of Tanabe and Sugano[8] we obtain the ligand field parameters, listed in Table II. The magnitude of Δ_t indicates a remarkably low tetrahedral field for the complex containing the transformed (*cis*) ligand, while B' is unexpectedly high for a sulfur donor ligand. However, the relatively low oscillator strength of the ν_3 band correlates with high values of B'.[11]

The values of the ligand field parameters of the *cis* ligand may be accounted for by assuming that in the brownish tetrahedral (or pseudo-tetrahedral) species the Co(II) to sulfur distance is larger than in the "normal" blue to tetrakis cation containing the nontransformed (*trans*) ligand. This can be rationalized in terms of repulsion between ligand molecules, which apparently is greater for complexes containing the *cis* than for those containing the *trans* ligand. In agreement with this, it it interesting to note that DPTU interacts with cobalt(II) chloride in acetone to give a blue solution, which does not change on standing. The features of the visible spectrum of the blue solution are very similar to those of the analogous thiourea[1] and ethylenethiourea[2] complexes. This behavior suggests that both forms have analogous coordinating tendencies in the blue species, as would be expected for a drastic reduction in the steric interactions between ligands passing from [Co(DPTU)$_4$]$^{+2}$ to [Co(DPTU)$_2$Cl$_2$].

TABLE II

ELECTRONIC STRUCTURE PARAMETERS FOR THE Co(II)–DPTU COMPLEXES IN ACETONE

Parameters	[Co(DPTU)$_4$]$^{+2}$ blue	[Co(DPTU)$_4$]$^{+2}$ brown
ν_2, cm.$^{-1}$	7,200	4,500
ν_3, cm.$^{-1}$	14,500	14,500
$f(\nu_2) \times 10^3$	2.98	. . .
$f(\nu_3) \times 10^3$	11.1	4.03
Δ_t, cm.$^{-1}$	4,250	2,600
B', cm.$^{-1}$	600	830
ΔB, cm.$^{-1}$ (β)^a	367 (0.62)	146 (0.85)

^{a} B for the gaseous Co(II) ion = 976 cm.$^{-1}$, B = 976 − B', and $\beta = B'/976$.

The results obtained for the DPTU ligand in acetone and DMF clarify to some extent the observed behavior of the DCTU complexes in these solvents. Thus, comparing Figure 4 with Figure 3, it may be noted that the spectrum of the brownish transformed species [Co(DPTU)$_4$]$^{+2}$ in acetone is very close to that of the DMF solution of [Co(DCTU)$_6$]X$_2$ containing a large excess of free DCTU, in which [Co(DCTU)$_4$]$^{+2}$ is the principal species. Further, the spectrum of the second species responsible for the isosbestic point at 14,550 cm.$^{-1}$ during the transformation of the blue species [Co(DPTU)$_4$]$^{+2}$ (Figure 4) compares well with the spectrum of a saturated solution of [Co(DCTU)$_6$]X$_2$ (X = NO$_3$, ClO$_4$) in acetone (Figure 2). This similarity suggests that an analogous structural change, namely *cis–trans* isomerism, is involved in the acetone and DMF solutions of DCTU. The slow precipitation of [Co(DCTU)$_6$]X$_2$ from its acetone solutions upon addition of a large excess of free ligand now can be understood by assuming that the solid six-coordinated complexes contain the transformed rather than the stable (*trans*) form. This assumption also explains the features of the spectra of the saturated solutions of the complexes, which evidently are consistent with the presence of both the transformed and original species [Co(DCTU)$_4$]$^{+2}$ in equilibrium (compare Figure 2 with Figure 4).

The solid compounds [Co(DCTU)$_6$]X$_2$ (X = NO$_3$, ClO$_4$) are, to the authors' knowledge, the first examples of six-coordinated Co(II) complexes containing solely unidentate sulfur ligands. This result is unexpected since from both steric and polarizability considerations one should expect that thiourea ligands with bulky N-substituents would favor the formation of tetrahedral complexes preferentially. In our case, it seems probable that because of the hindered ap-

[11] F. A. Cotton and R. H. Soderberg, *J. Am. Chem. Soc.*, **84**, 872 (1962).

Table III

Analytical Data

Compound	% C Calcd.	% C Found	% H Calcd.	% H Found	% N Calcd.	% N Found	% Cl Calcd.	% Cl Found
$[Co(DCTU)_6](NO_3)_2$	57.6	57.4	8.9	8.8	12.1	12.3		
$[Co(DCTU)_6](ClO_4)_2$	55.1	54.6	8.5	8.6	9.9	9.6		
$[Ni(DCTU)_5](ClO_4)_2$	55.1	55.5	8.5	8.6	9.9	9.4		
$[Co(DCTU)_2Cl_2]$	51.5	51.5	7.9	8.1	9.2	8.9	11.6	11.4
$[Co(DCTU)_2(NCS)_2]$	51.3	51.7	7.4	7.4	12.8	12.5		
DCTU (Fluka, AG. Purum)	64.94	64.87	10.06	9.77				

proach of the sulfur donor atom in the tetrakis species containing the transformed (*cis*) form of the ligand, a relatively high positive charge would remain on the central atom. Hence, the formation of six-coordinated species might be favored in order to satisfy the electroneutrality principle. Of course, steric effects also may be operative in the $[Co(DCTU)_6]X_2$ complexes, as shown by the somewhat lower value of Δ_0 in comparison with other thioureas.[1]

Finally, it is noteworthy that the blue solid derivatives $[Co(DCTU)_2X_2]$ (X = Cl, NCS) are "normal" tetrahedral species, as indicated by the spectral data in Table I.[1,3]

Experimental

Preparation of Compounds.—All complexes were readily prepared in yields $\geq 70\%$ by refluxing in ethyl alcohol stoichiometric amounts of the appropriate metal salt andD CTU. The solid complexes, obtained by cooling the hot reaction mixture, were suction filtered, washed several times with small amounts of cold acetone, and dried under vacuum. The analytical data are given in Table III.

Attempted Preparation of the DPTU Complexes.—Attempts were made to prepare these complexes from the appropriate Co(II) salt and DPTU in several solvents. In all cases, a large excess of free ligand was necessary in order to obtain species containing the coordinated ligand. Evaporation of the solutions led to concurrent separation of free DPTU. The pure complexes could not be obtained by recrystallization of the mixtures that were isolated.

Instrumentation.—Infrared spectra were obtained with a Beckman IR-5 spectrophotometer with sodium chloride optics.

Ultraviolet and visible spectra were obtained using a Perkin-Elmer Model 137 ultraviolet spectrophotometer. Diffuse reflectance spectra were recorded by use of a standard attachment to the same spectrophotometer and magnesium carbonate as a reference reflector. Near-infrared spectra were performed on Nujol mulls[12] and recorded on a Beckman DK-2 spectrophotometer.

Conductance measurements were made with an Industrial Instruments, Inc., Model RC 16 B 2 conductivity bridge.

A Gouy magnetic balance was used to determine magnetic susceptibilities. The Gouy tubes were calibrated using $Hg[Co(NCS)_4]$. The determination and calculation of magnetic susceptibilities were performed at room temperature, according to the directions of Figgis and Lewis.[13]

X-Ray powder patterns were obtained utilizing cobalt and copper $K\alpha_1$ radiations. Pertinent data are collected in Table IV.

Table IV

X-Ray Powder Data[a]

$[Co(DCTU)_6]-(ClO_4)_2$	$[Ni(DCTU)_6]-(ClO_4)_2$	$[Co(DCTU)_6]-(NO_3)_2$	$[Ni(DCTU)_6]-(NO_3)_2$
8.67 s	8.67 s	9.17 s	9.17 s
6.19 m	6.19 m	5.95 m	5.89 m
4.87 vs	4.87 vs	4.61 vs	4.63 vs
4.21 m	4.20 m	4.27 m	4.28 m
3.99 m	4.02 m	3.93 m	3.93 m
3.68 s	3.70 s	3.56 s	3.55 s
3.26 w	3.21 w	3.23 w	3.20 w
2.78 w	2.79 w	3.03 w	3.03 w
2.49 w	2.52 w	2.86 w	2.87 w

[a] Data are interplanar spacings calculated from the more prominent lines in the range $8° \leq 2\theta \leq 37°$. Relative intensities are listed (vs, very strong; s, strong; m, medium; w, weak).

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[13] B. N. Figgis and J. Lewis, "Modern Co-ordination Chemistry," Interscience Publishers, New York, N. Y., 1960, p. 416.