Reactivity of 1,1-Dithiolato Ni(II) and Co(II) with Phenylthiourea, Chlorophenylthiourea and Bis(diphenylphosphinothioyl)methane

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The following mixed ligand complexes were synthesized and characterized: $\text{Co(Phdtcz)}_2(\text{Phtu})_2$, $\text{Co(Phdtcz)}_2(\text{Clphtu})_2$, $\text{Co(Phdtcz)}_2(\text{dtm})$, $\text{Ni(Et}_2\text{dtc)}_2(\text{dtm})$, $\text{Ni(Phdtc)}_2(\text{dtm})$, $\text{Ni}(p\text{-Toluiddtc)}_2(\text{dtm})$, $\text{Ni}(\alpha\text{-naphdtc)}_2(\text{dtm})$, and $\text{Ni(Phdtcz)(Et}_2\text{dtc)}$; where Phdtcz = phenyldithiocarbamate, Et_2dtc = diethyldithiocarbamate, Phdtc = phenyldithiocarbamate, $p\text{-Toluiddtc}$ = p -toluidinedithiocarbamate, $\alpha\text{-naphdtc}$ = α -naphthyldithiocarbamate, Phtu = phenylthiourea, Clphtu = chlorophenylthiourea, and dtm = bis(diphenylphosphinothioyl)methane. Electronic and IR spectra, magnetic, conductivity and X-ray powder diffraction measurements were carried out. The Ni(II) and Co(II) complexes are suggested to be square planar and octahedral, respectively. The biological activity of the complexes was also tested.

Introduction

Current interest in the preparation of dithiocarbamate and dithiocarbamate complexes of transition metals and their reactivity with different Lewis bases [1–3] has prompted this report on the interaction of some dithiocarbamate and dithiocarbamate complexes of Co(II) and Ni(II) with sulphur containing ligands including phenylthiourea (PhNHCSNH_2), chlorophenylthiourea (ClPhNHCSNH_2), and bis(diphenylphosphinothioyl)methane [$\text{Ph}_2\text{P(S)CH}_2\text{P(S)Ph}_2$]. The last ligand and other related compounds and their complexes were the subject of recent papers [4–6].

Results and Discussion

The complexes (Table I) are obtained readily from the interaction of dithiocarbamate and dithiocarbamate Co(II) with the respective ligands. The compounds are fairly soluble in most of the common organic solvents. Mixed ligand complexes with dtm are crystalline solids. The conductivity measurements of Co(II) mixed ligand complexes of Phtu and Clphtu in DMF (complexes **1** and **2**) reveal that they are essentially non-electrolytes. Complexes of Co(II) and Ni(II) with bis(diphenylphosphinothioyl)methane (compounds **3–7**) display conductivity values much lower than those expected for 1:1 electrolytes [7].

All Co(II) dithiocarbamate mixed ligand complexes exhibit magnetic moment values which seem to fall in the range expected for spin only octahedral Co(II) complexes [8]. Dithiocarbamate Ni(II) mixed ligand complexes with dtm are diamagnetic (Table II).

The electronic spectra of compounds **1–3** in acetone show a broad band in the region 17,540–18,510 cm^{-1} (Table II). It is characteristic of octahedral Co(II) complexes and can be assigned to the transition ${}^4\text{T}_{1g}(\text{P}) \rightarrow {}^4\text{T}_{1g}$. Bands in the range 37,000–40,000 cm^{-1} are ascribed to $\pi \rightarrow \pi^*$ transitions.

The electronic spectra of compounds **4–7** in acetone solutions display two bands in the range 15,600–17,800 cm^{-1} and 20,000–23,810 cm^{-1} , which are characteristic of square planar complexes. These bands seem to correspond to the transitions ${}^1\text{A}_{1g} \rightarrow {}^1\text{A}_{2g}$ and ${}^1\text{A}_{1g} \rightarrow {}^1\text{B}_{1g}$ [9], respectively. According to recent studies on square planar Ni(II) complexes [10] including $\text{Ni(Et}_2\text{dtc)}_2$ and $\text{Ni(Et}_2\text{dtp)}_2$ (where $\text{Et}_2\text{dtc} = \text{Et}_2\text{NCSS}^-$ and $\text{Et}_2\text{dtp} = (\text{EtO})_2\text{PSS}^-$), the two bands can be assigned to ${}^1\text{A}_{1g} \rightarrow {}^1\text{B}_{1g}$ ($x^2 - y^2$, xy) and ${}^1\text{A}_{1g} \rightarrow {}^1\text{B}_{1g}$ (z^2 , xy). In addition, bands at about 31,000 cm^{-1} can be considered as CT bands (maybe associated with $\text{Ni} \rightarrow \text{SC}^-$). Compound **5** shows, further, a band at 41,660 cm^{-1} assignable to an intramolecular charge transfer in the dtc ligand of the type $\pi \rightarrow \pi^*$ of the $\text{N} \cdots \text{C} \cdots \text{S}$ group [11]. The electronic spectra are thus compatible with the diamagnetic nature of these complexes, and confirm their square planar structure.

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No.	Complex	S [%] Found (Calcd)	N [%] Found (Calcd)	m.p. (°C)	Yield [%]
1	Co(Phdtcz) ₂ (Phtu) ₂	26.22 (26.35)	15.29 (15.35)	275	45
2	Co(Phdtcz) ₂ (Clphtu) ₂	23.86 (24.08)	13.91 (14.02)	245	55
3	Co(Phdtcz) ₂ (dtm)	21.90 (22.01)	6.37 (6.41)	160	60
4	Ni(Et ₂ dtc) ₂ (dtm)	23.83 (23.93)	3.53 (3.48)	170	80
5	Ni(Phdtc) ₂ (dtm)	22.72 (22.80)	3.23 (3.31)	175	70
6	Ni(<i>p</i> -Toluidtc) ₂ (dtm)	21.93 (22.06)	3.19 (3.21)	170	60
7	Ni(α -Naphdtc) ₂ (dtm)	20.24 (20.38)	2.85 (2.96)	180	55
8	Ni(Phdtcz)(Et ₂ dtcm)	32.71 (32.86)	10.62 (10.76)	200	65

Table I. Analytical data and physical properties of the complexes.

Table II. Magnetic moments and electronic spectral data of the complexes (in cm⁻¹).

Com- pound	$\nu_{\max}$	Assignment	μ_{eff} (B. M.)
1	18,510 37,030	$^4T_{1g} \rightarrow ^4T_{1g}$ (P) $\pi-\pi^*$	3.81
2	18,180 37,030	$^4T_{1g} \rightarrow ^4T_{1g}$ (P) $\pi-\pi^*$	3.88
3	17,550 40,000	$^4T_{1g} \rightarrow ^4T_{1g}$ (P) $\pi-\pi^*$	3.82
4	15,870 20,270 30,580	$^1A_{1g} \rightarrow ^1B_{1g}$ (x^2-y^2 , xy) $^1A_{1g} \rightarrow ^1B_{1g}$ (z^2 , xy) CT	Dia
5	15,500 — 31,940 41,660	$^1A_{1g} \rightarrow ^1B_{1g}$ (x^2-y^2 , xy) — CT $\pi-\pi^*$	Dia
6	15,625 — 32,250	$^1A_{1g} \rightarrow ^1B_{1g}$ (x^2-y^2 , xy) — CT	Dia
7	18,510 31,250	$^1A_{1g} \rightarrow ^1B_{1g}$ (x^2-y^2 , xy) CT	Dia
8	19,410 23,350 30,486	$^1A_{1g} \rightarrow ^1B_{1g}$ (x^2-y^2 , xy) $^1A_{1g} \rightarrow ^1B_{1g}$ (z^2 , xy) CT	Dia

The IR spectra of compounds **1** and **2** show a splitting of νCSS of the dithiocarbamate moiety, which may indicate a change of coordination mode of dithiocarbamate from SS $\rightarrow$ SN [2].

The IR spectrum of compound **3** shows a split band at 990 and 1020 cm⁻¹ (νCSS) suggesting coordination of phenyldithiocarbamate ligands through S and N atoms. The bonding of dtm to the cobalt ion is evident by the red shift observed for $\nu\text{P}=\text{S}$ (615–620 cm⁻¹) with respect to the free ligand (628 cm⁻¹) [6]. The complex shows νCoS at 360 and 340 cm⁻¹, and νCN at 1340 cm⁻¹ (Table III).

Passing to Ni(II) dithiocarbamate mixed ligand complexes with dtm, we have found that compounds **6** and **7** display νCSS as a split band in the region 990–1010 cm⁻¹, while compounds **4** and **5** exhibit in this frequency range a broad unresolved band, indicating the monodentate nature of the dithiocarbamate anion in these complexes. Furthermore, νCN appears in the range 1385–1435 cm⁻¹ and at almost the same frequency as in the parent Ni(II) dithiocarbamate complexes. $\nu\text{P}=\text{S}$ occurs for these complexes in the 590–620 cm⁻¹ region of the spectrum, indicating a metal-sulphur bonding. A band in the range 370–395 cm⁻¹, which is sometimes associated with a shoulder (suggesting the presence of two types of Ni–S bond), can be tentatively assigned as $\nu\text{Ni}-\text{S}$.

The X-ray powder diffraction patterns for compounds **4** and **5** (as representatives) indicate that these two mixed ligand complexes are nearly isomorphous with related phosphine mixed ligand complexes of dithiocarbamate Ni(II), for which square planar structures and monodentate dithiocarbamates have been suggested [12] (Table IV).

Table III. Important IR bands of the complexes.

	1	2	3	4	5	6	7	8
ν CSS	1010, 1030	1010, 1030	1000, 1020	1010 (broad)	990 (broad)	990, 1010	990, 1010	990
ν CN	1360	1420	1340	1380	1400	1400	1305	1335, 1350
ν P=S	—	—	615	600	590, 610	620	620	—
ν Cos	—	—	360, 340 sh	—	—	—	—	—
ν NiS	—	—	—	385, 375 sh	380, 370 sh	385	380, 370 sh	380

Table IV. X-ray powder patterns (d-spacings, Å)^a.

Ni(Et ₂ dtc) ₂ (dtm)	Ni(Phdtc) ₂ (dtm)	Ni(α -naphdtc) ₂ (dpp) ₂ ^b	Ni(Phdtc) ₂ (dpe) ₂ ^b
10.6 s	11.1 s	11.05 vs	—
9.2 w	—	—	9.8 w
8.1 vs	8.2 m	8.8 w	—
7.1 w	7.1 w	—	7.3 m
6.3 w	6.5 w	6.8 w	6.8 w
5.8 w	5.3 w	6.3 w	6.3 w
5.1 m	4.9 w	5.9 w	5.5 w
4.6 w	4.6 w	4.4 m	4.6 s
4.2 w	4.3 w	4.2 s	4.4 m
4.1 w	4.1 w	—	4.2 w
4.0 w	3.9 w	3.7 w	4.0 w

^a Intensities were estimated visually;^b from reference [12]; dpe = bis(diphenylphosphino)ethane; dpp = bis(diphenylphosphino)propane.

We have attempted to prepare a mixed ligand complex from the interaction of sodium diethyldithiocarbamate and bis(phenyldithiocarbazato)-nickel(II), but only the dithiocarbamate complex was obtained as the final product:

The resulting complex is identified on the basis of microanalysis, IR and electronic spectra. The mixed ligand complex could, however, be obtained through the reaction of bis(diethyldithiocarbamato)nickel(II) and bis(phenyldithiocarbazato)nickel(II).

This complex has been proved to be diamagnetic. The acetone solution of the complex shows two d-d bands in its electronic spectrum at 19,410 and 23,250 cm⁻¹; the position and shape of the bands is

typical of a square planar stereochemistry. The two bands are shifted to higher energies as compared with those of bis(diethyldithiocarbamato)nickel(II) or bis(phenyldithiocarbazato)nickel(II) in acetone.

The IR spectrum exhibits the characteristics of both diethyldithiocarbamate and dithiocarbazate anions. Thus the mixed ligand complex shows two bands at 1350 cm⁻¹ and 1335 cm⁻¹ (shoulder), which correspond to ν CN of dithiocarbazate [1] and dithiocarbamate [13], respectively. The band of medium intensity observed at 990 cm⁻¹ is assigned to the C=S stretching vibration. Of particular importance are the bands in the range 2830–2960 cm⁻¹ and 680–700 cm⁻¹, which correspond to ν CH-stretching vibrations of the ethyl groups of diethyldithiocarbamate and the frequencies of the monosubstituted phenyl group of the phenyldithiocarbazate moiety, respectively.

The biological activities of some of the mixed ligand complexes were tested against a number of bacteria *vz.*, *E. coli*, *St. albus*, *M. luteus*, and *B. subtilis*. Compounds **1** and **5** show variable anti-

bacterial activities against the test bacteria, but with compounds **3**, **4** and **6** no reaction is observed (Table V).

Table V. Antimicrobial screening of some of the complexes.

Test bacteria	1	3	4	5	6
<i>E. coli</i>	++	—	—	—	—
<i>St. albus</i>	+	—	—	+	—
<i>M. luteus</i>	+++	—	—	—	—
<i>B. subtilis</i>	+++	—	—	+	—

Weak +; Medium ++; Strong +++; Resistant —.

Experimental

Bis(phenyldithiocarbazato)cobalt(II), bis(phenyldithiocarbazato)nickel(II) [1], bis(diethyldithiocarbamato)nickel(II) [14], bis(phenyldithiocarbamato)nickel(II), bis(*p*-toluidinedithiocarbamato)nickel(II) [15], bis(α -naphthyldithiocarbamato)nickel(II) [13], and bis(diphenylphosphinothiyl)methane [16] were prepared according to literature procedures.

Co(Phdtcz)₂(Phtu)₂ and Co(Phdtcz)₂(Clphtu)₂

A solution of 0.33 g (2.4 mmole) phenylthiourea in ethanol was added to a solution of 0.5 g (1.2 mmole) bis(phenyldithiocarbazato)cobalt(II) in acetone. This mixture was refluxed for about 3 h. A black precipitate was formed, which was filtered, washed with ethanol and dried *in vacuo* over P₂O₅. In a similar manner Co(Phdtcz)₂(Clphtu)₂ was prepared.

Co(Phdtcz)₂(dtm)

An alcoholic solution containing 0.53 g (1.2 mmole) bis(diphenylphosphinothiyl)methane was added dropwise with stirring to a solution of 0.5 g (1.2 mmole) bis(phenyldithiocarbazato)cobalt(II) in ethanol. The mixture was refluxed for 2 h whereupon a brown precipitate was formed, which was filtered, washed with alcohol and then dried *in vacuo* over P₂O₅.

General method for the preparation of dithiocarbamato nickel(II) complexes with dtm

The preparation of the complexes was achieved *via* the following procedure: A chloroform solution of bis(diphenylphosphinothiyl)methane (1.2 mmole) was added dropwise under continuous stirring to an equivalent amount of a chloroform solution of the dithiocarbamato nickel(II) complex (1.2 mmole). The mixture was left stirring at room temperature for 3 h, concentrated by slow evaporation of the solvent followed by standing overnight. The dark to pale green crystals (violet in case of compound **7**) were filtered, washed with little chloroform, and dried *in vacuo* over P₂O₅.

Ni(Et₂dte)(Pdhtcz)

A chloroform solution of bis(phenyldithiocarbazato)nickel(II) (2.4 mmole) was mixed with a chloroform solution of bis(diethyldithiocarbamato)nickel(II) (2.4 mmole), and the mixture was refluxed for 5 h. Concentrating the solution to about one third of the volume produced a dark brown product (almost black), which was filtered, washed with little chloroform, and dried *in vacuo* over P₂O₅.

Reaction of Ni(Phdtcz)₂ and NaEt₂dte

An ethanolic solution of Ni(Phdtcz)₂ was treated with sodium diethyldithiocarbamate dissolved in ethanol (1:1 mole ratio), and the mixture refluxed for 2 h. The green precipitate was filtered, washed with little ethanol, and dried *in vacuo* over P₂O₅.

Physical measurements

The conductivity in DMF solutions was measured with an LF Digi 550 conductance bridge at 25 °C. The magnetic moments were obtained with the Gouy balance using Co[Hg(NCS)₄] as the calibrant. Electronic spectra in solution were recorded on a Shimadzu UV-200S spectrophotometer. The infrared spectra in the range 4000–200 cm^{−1} were measured in KBr pellets on a Perkin Elmer 599B spectrophotometer. Powder diffraction patterns were recorded on a Shimadzu X-ray diffraction unit with a CuK α target (λ = 1.54 Å).

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- [1] B. B. Kaul and K. B. Pandeya, *J. Inorg. Nucl. Chem.* **40**, 1035 (1978); and references therein.
- [2] A. A. M. Aly, M. M. Kamal, M. S. El Meligy, and A. I. El Said, *Z. Naturforsch.* **39b**, 1676 (1984); and references therein.
- [3] a) G. A. Katsoulos, G. E. Manoussakis, and C. A. Isipis, *Polyhedron* **3**, 735 (1984);
b) R. Schierl, U. Nagel, and W. Beck, *Z. Naturforsch.* **39b**, 649 (1984);
c) K. J. Cavell, R. J. Magee, and J. O. Hill, *J. Inorg. Nucl. Chem.* **41**, 1281 (1979);
d) W. Beck, M. Girnth, M. Castillo, and H. Zippel, *Chem. Ber.* **111**, 1246 (1978).
- [4] S. O. Grim, S. Nittolo, N. L. Ammon, P. H. Smith, I. J. Colquhoun, and W. McFarlane, *Inorg. Chim. Acta* **77**, L, 241 (1983).
- [5] E. W. Ainscough and A. M. Brodie, *Coord. Chem. Rev.* **27**, 59 (1978) and references therein.
- [6] E. W. Ainscough, H. A. Bergen, and M. Brodie, *J. Chem. Soc. Dalton* **1976**, 1649.
- [7] W. J. Geary, *Coord. Chem. Rev.* **7**, 81 (1971).
- [8] *Modern Coordination Chemistry*, Interscience Publishers Ltd., London 1960, p. 406.
- [9] A. B. P. Lever, *Inorganic Electronic Spectroscopy*, Elsevier, Amsterdam 1968.
- [10] M. A. Atanassov and G. St. Nikolov, *Inorg. Chim. Acta* **68**, 15 (1983).
- [11] G. C. Franchini, A. Giusti, C. Preti, L. Tassia, and P. Zannini, *Polyhedron* **4**, 1553 (1985).
- [12] A. A. M. Aly, A. A. Mohamed, M. A. Mousa, and M. El-Shabasy, *Chem. Scripta* **24**, 196 (1984).
- [13] B. B. Kaul and K. B. Pandeya, *J. Inorg. Nucl. Chem.* **40**, 229 (1978).
- [14] M. Umar Fayyaz and M. W. Grant, *Aust. J. Chem.* **32**, 2159 (1979).
- [15] D. Coucouvanis and J. P. Fackler (Jr.), *Inorg. Chem.* **6**, 2047 (1967).
- [16] W. E. Slinkard and D. W. Meek, *J. Chem. Soc. Dalton* **1973**, 1024.